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FORMATION OF "BLACK ALKALI" (SODIUM CARBONATE) IN CALCAREOUS SOILS

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INTRODUCTION

It is unfortunate that the term "alkali," when used to designate an accumulation of water-soluble salts in the soil, has come into such common use in the United States. In this paper, this term will be adhered to out of deference to common custom. The term will be used to designate sodium chlorid, sodium sulphate, sodium carbonate, or any of the other water-soluble salts of the soil. As is well known, the term "black alkali" originated from the fact that sodium carbonate acts upon the organic matter of the soil and produces a dark-colored solution.

The writer is aware of the fact that the presence of calcium carbonate is not necessary in all cases to explain the formation of sodium carbonate. In the decomposition of the basalts, alkaline carbonates are likely to be formed. These carbonates may be transported and may reappear in other areas. The alkaline marshes around Klamath, Oreg., are examples of this type of alkali that quite likely did not form in that place. It is the purpose of this paper to discuss only one specific phase of alkali formation, and that is that which takes place when sodium salts are present in a calcareous soil.

With the exception of an adequate water supply, the presence and accumulation of alkali is probably the most important problem that confronts the man engaged in farming under irrigation in the arid and semiarid regions of the West. The successful reclamation of desert lands is by no means an easy matter, and the handling of the soluble salts that have accumulated in the soil during the centuries that it has been lying in this arid condition offers many difficult problems.

As ordinarily used, the term "alkali" consists chiefly of the salts of sodium, together with in lesser amounts the salts of calcium and mag-

nesium. In this paper the term will be used to include all the water-soluble salts of the soil, whether organic or inorganic.

The alkali tolerance of the plant varies widely. For instance, a plant may thrive in a saturated solution of gypsum and be killed by 1 part per million of copper, or even by lesser amounts of some of the more toxic organic salts. The accumulation of alkali in the soil, therefore, in sufficient amounts to make agriculture impossible does not necessarily mean the accumulation of the salts of sodium, calcium, and magnesium.

In 1892, Dorsey (3)[1] estimated that about 847,000 acres of the irrigated land in the United States had already been lost by alkali accumulation. He placed a value of $50 an acre on this land, and calculated a loss of $42,000,000 on account of alkali accumulation. A valuation of $50 an acre seems reasonable, as this would hardly pay for the average reclamation and water right. This was 14 years ago and the evil has been increasing year by year since that time; $100,000,000 would probably not now cover the loss sustained by alkali during our brief experience in irrigation agriculture.

The loss of land by alkali accumulation might well be divided into two distinct classes: The first, or greatest loss, generally occurs when the soils are first brought under irrigation. Water is applied to the soils on the benches or higher levels, usually in excessive amounts, and this dissolves out the salts that have accumulated in the soil while in a desert condition. The water, carrying with it the salt, gradually finds its way to the lower levels and to the lower drainage basins, and upon evaporation leaves the dissolved salts on, or near, the surface. These salts are ordinarily largely sodium chlorid, sodium sulphate, sodium carbonate, and sodium bicarbonate This seepage takes place when there is an abundance of water and drainage from the higher to the lower levels, and it is probably responsible for 90 per cent of the loss that has been sustained in the irrigation projects of the United States up to date.

The alkali accumulation, which might be considered as secondary, is much slower and takes place upon the bench lands, as well as upon the lower levels, and also upon many areas where there is a limited amount of irrigation water, and no drainage or seepage. This phase of alkali accumulation will be taken up later.

FORMATION OF "BLACK ALKALI"

In the arid and semiarid regions of the West, where alkali conditions abound, the presence of calcium carbonate, or carbonate of lime, is so common that it has been termed by Dr. Hilgard "a standing characteristic" of alkali soil. In a great many cases, although the carbonate is not in evidence upon the surface of the soil, it may be found from a few inches to a few feet below the surface, acting as a cementing material in the troublesome hardpan. This hardpan usually occurs at the lower

[1] Reference is made by number to "Literature cited," p. 589.

edge of the moisture plane, or where the moist soil of the surface shades into the dry subsoil. While it is quite likely that capillarity had little or nothing to do in the formation of this hardpan, which occurred under conditions of limited rainfall, it is, however, usually within easy reach from the surface of the capillary pull which would occur in a saturated soil, especially under conditions of irrigation. The importance of this calcareous hardpan in the study of the formation of black alkali will be brought up later.

Of all the alkali elements existing in this area, sodium, occurring as sodium chlorid, sodium sulphate, sodium carbonate, or sodium bicarbonate, and sodium nitrate, is the most common. This is due to the fact that soils originated largely by the evaporation of marine lagoons or landlocked seas, or were derived primarily from the so-called granites or more properly, diorite (soda-lime feldspar and hornblende). In these same soils, except in cases where a too high salt content prohibits activity, nitrification is usually rather intense. The presence and accumulation of nitrates, from this as well as from other sources, is usually noticeable in such cases.

Sodium carbonate (black alkali) is frequently met with in this area. As this is the most toxic salt that exists in appreciable amounts in alkali soils, its origin has created a good deal of speculation. It seems probable that all cases of black alkali are not due to the processes of rock disintegration. While the toxic action of sodium carbonate upon plants is much greater than that of sodium bicarbonate, they will not be differentiated in this discussion. It must be remembered that sodium bicarbonate is formed from sodium carbonate by the addition of carbon dioxid. Any cause which will liberate the carbon dioxid, such as the precipitation of the salt upon the surface by the evaporation of the water in which it is dissolved, will tend to convert the bicarbonate to the carbonate. The natural tendency of the bicarbonate is to become a carbonate, and, as carbon dioxid exists in all soils in appreciable amounts, it seems probable that the primary step in the formation of black alkali is often the formation of sodium carbonate.

REACTION BETWEEN SODIUM SALTS AND CALCIUM CARBONATE

It is well known that sodium salts will react with calcium carbonate, with the formation of sodium carbonate or bicarbonate and the corresponding calcium salt. The extent of this reaction and its bearing upon the formation of black alkali in nature has been taken up in this investigation.

Cameron (1) has described the probable formation of different types of alkali, and later Seidell (2), working under his direction, studied the reaction between sodium chlorid, sodium sulphate, and calcium carbonate. They drew air through the solutions until they had reached equilibrium and determined the amounts of sodium bicarbonate thus formed.

Hilgard, working with Webber, and later with Jaffa, determined the amounts of sodium bicarbonate formed when a stream of carbon dioxid was passed through solutions of sodium sulphate and sodium chlorid in contact with an excess of calcium carbonate (6, p. 449–451).

The solubility of calcium carbonate in pure water is about 10 parts per million, while in the presence of carbon dioxid its solubility is increased many times. In boiled distilled water calcium carbonate may be titrated, phenolphthalein being used as an indicator. However, the amount of carbon dioxid that usually occurs in ordinary distilled water is sufficient to make such a titration impossible. In such a case the titration with methyl orange as an indicator will, of course, give the amount of lime.

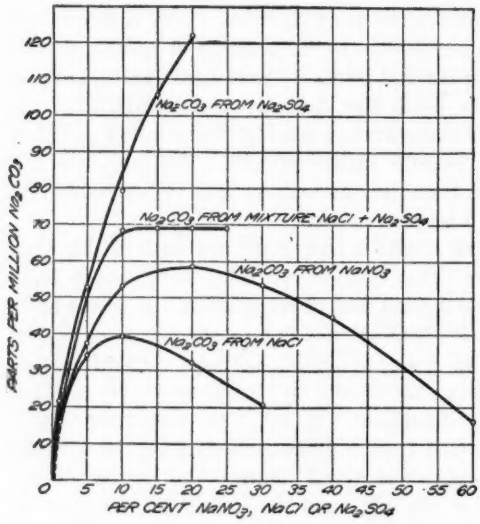

FIG 1.—Graphs of the sodium carbonate formed from reaction of calcium carbonate (solid phase present) with sodium chlorid, sodium nitrate, or sodium sulphate.

In this investigation the results of the reactions of sodium nitrate, sodium chlorid, and sodium sulphate with calcium carbonate, which react with phenolphthalein, are figured as sodium carbonate, while all titrations which react with methyl orange are figured as sodium bicarbonate. While it is realized that this is not strictly accurate, from the standpoint of a physical chemist, yet it is sufficiently accurate for the purposes of this investigation.

Occasional samples of a salt, especially sodium chlorid and sodium sulphate, were found to be slightly acid. This caused a great deal of trouble until the cause was discovered. Afterwards all salt solutions were neutralized with sodium hydrate before beginning the experiments.

This work was done at Riverside, Cal., and apparatus for the accurate control of temperature was not at hand. The work was carried on at room temperatures, with a considerable variation between night and day. The determinations, therefore, must not be understood as solubility measurements, but simply laboratory studies to be applied to field conditions near by.

The formation and the accumulation of nitrates and their effect upon plants has recently been given much attention, especially by the Califor-

nia, Colorado, and Utah Experiment Stations. Owing to the interest in this subject and in the injurious effects of continued applications of sodium nitrate as a fertilizer to Citrus groves, the reaction of sodium nitrate and calcium carbonate was first considered.

Solutions of sodium nitrate in graduated concentrations (given in Table I) were prepared with boiled distilled water. These were put in shaker bottles, with about 1 gm. of calcium carbonate in each bottle, tightly stoppered, and shaken for several days, or until they had reached equilibrium. Special effort was made to keep carbon dioxid out of the solution, but the opening of the bottle for the purpose of titrations, etc., made it impossible to keep it entirely out. As the saturation point of sodium nitrate increases noticeably with an increase of temperature, 60 per cent was taken as approximately representing the average condition of saturation.

When equilibrium was reached, aliquots were drawn off and titrations made for carbonates, with phenolphthalein as an indicator. The titration in distilled water, which was, of course, due to calcium carbonate was subtracted from each of the other titrations where sodium nitrate was present. This difference was then calculated as sodium carbonate. These results are shown in Table I and figure 1.

TABLE I.—*Reaction between sodium nitrate and calcium carbonate*

Solution No.	Percentage of sodium nitrate.	Quantity of *N*/20 sulphuric acid for 100 c. c. of solution.	Parts per million of sodium carbonate formed.	Solution No.	Percentage of sodium nitrate.	Quantity of *N*/20 sulphuric acid for 100 c. c. of solution.	Parts per million of sodium carbonate formed.
		C. c.				*C. c.*	
1	0	0.3	0.0	5	20	1.4	58.3
2	1	.6	15.9	6	30	1.3	53.0
3	5	1.0	37.1	7	40	1.15	45.0
4	10	1.3	53.0	8	60	.6	15.9

Solutions of sodium chlorid and sodium sulphate and mixtures of equal parts of sodium chlorid and sodium sulphate were prepared and run in the same way as with the sodium nitrate. These results are shown in Tables II, III, and IV and figure 1.

TABLE II.—*Reaction between sodium chlorid and calcium carbonate*

Solution No.	Percentage of sodium chlorid.	Quantity of *N*/20 sulphuric acid for 100 c. c. of solution.	Parts per million of sodium carbonate formed.	Solution No.	Percentage of sodium chlorid.	Quantity of *N*/20 sulphuric acid for 100 c. c. of solution.	Parts per million of sodium carbonate formed.
		C. c.				*C. c.*	
1	0	0.3	0.0	4	10	1.05	39.8
2	1	.6	15.9	5	20	.9	31.8
3	5	.95	34.4	6	30	.7	21.2

TABLE III.—*Reaction between sodium sulphate and calcium carbonate*

Solution No.	Percentage of sodium sulphate.	Quantity of *N*/20 sulphuric acid for 100 c. c. of solution.	Parts per million of sodium carbonate formed.	Solution No.	Percentage of sodium sulphate.	Quantity of *N*/20 sulphuric acid for 100 c. c. of solution.	Parts per million of sodium carbonate formed.
		C. c.				*C. c.*	
1.....	0	0.3	0.0	4.....	10	1.8	79.5
2.....	1	.7	21.2	5.....	15	2.3	106.0
3.....	5	1.3	53.0	6.....	20	2.6	122.0

TABLE IV.—*Reaction between mixtures of equal parts of sodium chlorid and sodium sulphate and calcium carbonate*

Solution No.	Percentage of mixture.	Quantity of *N*/20 sulphuric acid for 100 c. c. of solution.	Parts per million of sodium carbonate formed.	Solution No.	Percentage of mixture.	Quantity of *N*/20 sulphuric acid for 100 c. c. of solution.	Parts per million of sodium carbonate formed.
		C. c.				*C. c.*	
1.....	0	0.3	0.0	5.....	15	1.6	68.9
2.....	1	.6	15.9	6.....	20	1.6	68.9
3.....	5	1.3	53.0	7.....	25	1.6	68.9
4.....	10	1.6	68.9				

In the reaction $NaNO_3+CaCO_3 \rightleftarrows Na_2CO_3+Ca(NO_3)_2$, at a maximum of about 20 per cent of sodium nitrate there is a possibility of a formation of about 58 parts per million of sodium carbonate.

In the reaction $2NaCl+CaCO_3 \rightleftarrows Na_2CO_3+CaCl_2$, at a maximum concentration of about 10 per cent of sodium chlorid there is a possibility of a formation of about 40 parts per million of sodium carbonate.

In the reaction $Na_2SO_4+CaCO_3 \rightleftarrows Na_2CO_3+CaSO_4$, at the saturation point of sodium sulphate there is a possibility of the formation of about 122 parts per million of sodium carbonate under the conditions of this experiment.

The reactions just described are what might be termed the reverse reactions of those commonly considered when these salts are brought together. With sodium chlorid and calcium carbonate, for example, the reaction might be written $CaCl_2+Na_2CO_3 \rightleftarrows CaCO_3+2NaCl$; or calcium chlorid and sodium carbonate in equilibrium with calcium carbonate and sodium chlorid. No matter which combination of salts is used, the resulting system will be exactly the same, and in the reaction last described there would still be about 40 parts per million of sodium carbonate left after the reaction had run to an end.

The drop in the curves, when sodium nitrate and sodium chlorid are used, as the saturation point is approached, is noticeable. This drop will be seen in all the curves outlined in this paper wherever a reaction takes place between calcium carbonate and sodium nitrate or sodium chlorid. This is not the case with sodium sulphate. The curve with this salt rises uniformly until the saturation point is reached. This fact will be explained later.

EFFECT OF SOLUBLE LIME SALTS UPON THE FORMATION OF SODIUM CARBONATE

The quantity of sodium carbonate formed in the reaction of calcium carbonate with sodium sulphate is relatively large in comparison with that formed with sodium nitrate or sodium chlorid. It was suggested that this might be due to the fact that in the reaction with sodium nitrate and sodium chlorid very soluble salts of lime, calcium nitrate, and calcium chlorid are formed, while with sodium sulphate a relatively slightly soluble salt, gypsum, is formed. This has a practical significance from the fact, as first advised by Dr. Hilgard, that the application of gypsum will improve soils containing too much black alkali. This is simply a reversal of the reaction considered above, as follows: $Na_2CO_3 + CaSO_4 \rightleftarrows Na_2SO_4 + CaCO_3$.

The following tables and curves will show the concentration of the soluble salts of lime that are required to stop the reaction at its maximum.

TABLE V.—*Reaction between 20 per cent solutions of sodium nitrate and calcium carbonate in the presence of calcium nitrate*

Solution No.	Percentage of calcium nitrate.	Parts per million of of sodium carbonate formed.	Solution No.	Percentage of calcium nitrate.	Parts per million of of sodium carbonate formed.
1	0.0	74.2	6	0.150	7.9
2	.025	34.5	7	.200	5.3
3	.050	21.2	8	.400	2.6
4	.075	15.9	9	.800	Trace.
5	.100	10.6	10	1.000	0

TABLE VI.—*Reaction between 10 per cent solutions of sodium chlorid and calcium carbonate in the presence of calcium chlorid*

Solution No.	Percentage of calcium chlorid.	Parts per million of sodium carbonate formed.	Solution No.	Percentage of calcium chlorid.	Parts per million of sodium carbonate formed.
1	0.0	53.0	5	0.8	Trace.
2	.1	7.9	6	1.2	Trace.
3	.2	2.6	7	1.6	Trace.
4	.4	Trace.	8	2.0	Trace.

TABLE VII.—*Reaction between 20 per cent solutions of sodium sulphate and calcium carbonate in the presence of calcium sulphate*

Solution No.	Percentage of calcium sulphate.	Parts per million of sodium carbonate formed.	Solution No.	Percentage of calcium sulphate.	Parts per million of sodium carbonate formed.
1	0.0	122.0	4	0.105	37.0
2	.026	95.4	5	.210	23.8
3	.052	69.0			

Calcium nitrate was added to 20 per cent solutions of sodium nitrate in amounts shown in Table V, and these solutions were shaken up with an excess of calcium carbonate until they had reached equilibrium. The sodium carbonate was then determined.

Calcium chlorid was also added to 10 per cent solutions of sodium chlorid, and calcium sulphate to 20 per cent solutions of sodium sulphate in the same way. The curve with calcium chlorid follows very closely the curve with sodium nitrate. Eliminating for the present other modifying factors, it will be seen that in the presence of 0.5 per cent of either of the soluble lime salts, calcium chlorid or calcium sulphate, the quantity of sodium carbonate formed from the reaction of calcium carbonate with sodium chlorid or sodium nitrate, is very slight. In other words, if such reactions are responsible for the formation of normal sodium carbonate or black alkali in the soil, and it will be shown later that such reactions unquestionably do take place, even in the presence of the carbon dioxid of the soil, it is an essential condition that the calcium-chlorid content of the soil solution be reduced below 0.2 per cent and the calcium nitrate content below 0.5 per cent. The removal of the calcium chlorid and the calcium nitrate under natural conditions might result either from drainage or from surface evaporation. In the latter case the salts would be brought to the surface in solution and would accumulate as a crust or efflorescence. This is exactly what happens in nature. The calcium chlorid, or "slick spots," which are so often mistaken for black alkali and which are so common in the West, are no doubt formed in this way.

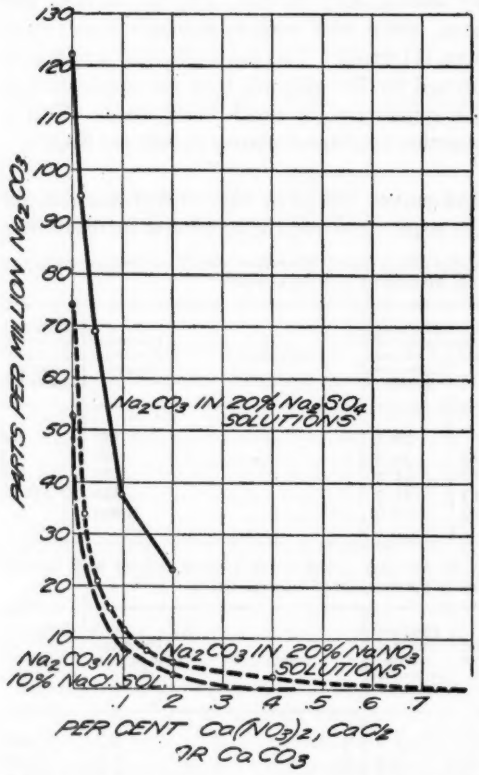

FIG. 2.—Graphs showing the depression of sodium carbonate formed by the reaction of calcium carbonate with sodium chlorid, sodium nitrate, or sodium sulphate when a soluble calcium salt containing a common anion is added.

On the other hand, there is an appreciable reaction between sodium sulphate and calcium carbonate, even in a saturated solution of calcium sulphate, as is shown in Table VII. The data in Tables V, VI, and VII are shown graphically in figure 2.

EFFECT OF GYPSUM UPON THE FORMATION OF SODIUM CARBONATE

As the soils of the West, as well as many of the irrigation waters, frequently contain gypsum in appreciable amounts, the reaction between the alkali salts sodium nitrate, sodium chlorid, and sodium sulphate with calcium carbonate usually takes place in the soil in the presence of more or less calcium sulphate. Tables VIII, IX, and X and figure 3 show the effect of this salt upon the formation of black alkali. As outlined in the tables, calcium sulphate was not added in excess, but a saturated solution containing 2.1 gm. per liter was used in preparing the different numbers. This was necessary in order to have a definite amount of calcium sulphate in the solutions, as the solubility of this salt increases very rapidly in the presence of certain sodium salts.

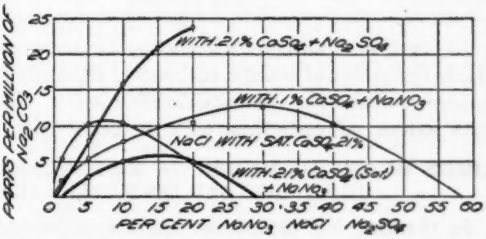
PARTS PER MILLION OF Na2CO3
25
20
15
10
5
WITH .21% CaSO4 + Na2SO4
WITH .1% CaSO4 + NaNO3
NaCl WITH SAT CaSO4 .21%
WITH .21% CaSO4 (Soil) + NaNO3
0 5 10 15 20 25 30 35 40 45 50 55 60
PER CENT NaNO3 NaCl Na2SO4

FIG. 3.—Graphs showing the effect of gypsum on the formation of sodium carbonate in the reaction of calcium carbonate with sodium chlorid, sodium nitrate, or sodum sulphate.

TABLE VIII.—*Reaction between sodium nitrate and calcium carbonate in the presence of calcium sulphate*

Solution No.	Percentage of sodium nitrate.	Parts per million of sodium carbonate in the presence of—		Solution No.	Percentage of sodium nitrate.	Parts per million of sodium carbonate in the presence of—	
		0.1 per cent of calcium sulphate.	0.21 per cent of calcium sulphate.			0.1 per cent of calcium sulphate.	0.21 per cent of calcium sulphate.
1	0	0.0	0.0	5	20	10.6	5.3
2	1	2.6	.0	6	30	13.2	.....
3	5	5.3	2.6	7	40	10.6	0.0
4	10	7.9	5.3	8	60	0.0	0.0

TABLE IX.—*Reaction between sodium chlorid and calcium carbonate in 0.21 per cent solutions of calcium sulphate*

Solution No.	Percentage of sodium chlorid.	Parts per million of sodium carbonate formed.	Solution No.	Percentage of sodium chlorid.	Parts per million of sodium carbonate formed.
1	0	0.0	4	10	10.6
2	1	5.3	5	20	5.3
3	5	10.6	6	30	0.0

TABLE X.—*Reaction between sodium sulphate and calcium carbonate in 0.21 per cent solutions of calcium sulphate*

Solution No.	Percentage of sodium sulphate.	Parts per million of sodium carbonate formed.	Solution No.	Percentage of sodium sulphate.	Parts per million of sodium carbonate formed.
1	0	0.0	4	10	15.9
2	1	Trace.	5	15	21.2
3	5	7.9	6	20	23.8

In the case of all three salts, at some concentration there is an appreciable formation of sodium carbonate, although gypsum is present in an amount sufficient to saturate distilled water. This is more pronounced with sodium sulphate than with the other salts.

LIMITS OF THE FORMATION OF SODIUM CARBONATE IN PRESENCE OF SOLUBLE AND INSOLUBLE SALTS OF LIME

In titrating out the sodium carbonate formed by the action of the sodium salts on calcium carbonate it was noted that the color with phenolphthalein soon began to reappear in the solutions when calcium carbonate was present after the titration had been finished, indicating the formation of more sodium carbonate. Under field conditions the sodium carbonate formed would tend to be neutralized or "titrated out" by reacting with the organic matter or silicates of the soil.

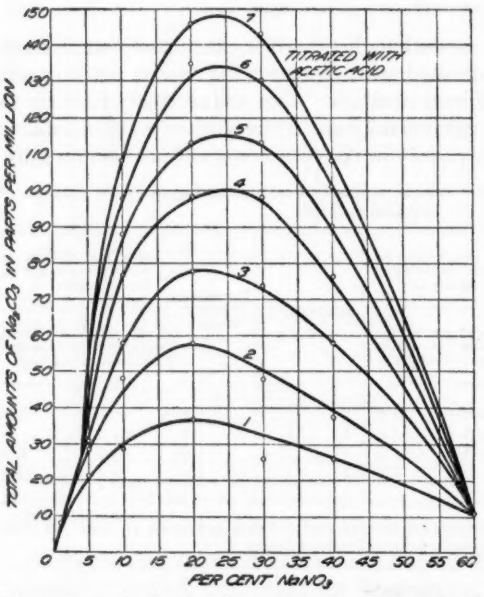

FIG. 4.—Graphs showing the sodium carbonate formed by reaction of calcium carbonate (solid phase present) with sodium nitrate. Sodium carbonate titrated out with acetic acid, allowing equilibrium to be established between successive titrations. Numbers refer to titrations. Each graph represents the total sodium carbonate neutralized up to and including that titration.

Acetic acid, representing a weak organic acid and one which gives a very soluble salt of lime, and oxalic acid, another weak acid which gives a very insoluble salt of lime, were taken in standard solutions and used instead of sulphuric acid to titrate out the sodium carbonate formed by the action of sodium nitrate and calcium carbonate. In a rough way

TABLE XI.—*Titrations with acetic acid of the sodium nitrate-calcium carbonate solution*

Solution No.	Strength of solution.	Parts per million of sodium carbonate (totals).						
		First titration.	Second titration.	Third titration.	Fourth titration.	Fifth titration.	Sixth titration.	Seventh titration.
1	Boiled water.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	1 per cent of sodium nitrate..	7.9	7.9	7.9	7.9	7.9	7.9	7.9
3	5 per cent of sodium nitrate..	21.2	29.1	29.1	34.4	34.4	34.4	34.4
4	10 per cent of sodium nitrate..	29.5	48.0	58.6	77.1	87.7	98.3	108.9
5	20 per cent of sodium nitrate..	37.1	58.3	79.5	98.0	113.9	135.1	145.7
6	30 per cent of sodium nitrate..	26.5	47.7	74.2	98.0	113.9	129.8	143.0
7	40 per cent of sodium nitrate..	26.5	37.1	58.3	76.8	90.0	103.2	108.5
8	60 per cent of sodium nitrate..	10.6	10.6	10.6	10.6	10.6	10.6	10.6

this was an imitation of the probable conditions existing in the field. When the color was titrated out of all the solutions, they were tightly stoppered and shaken until they had again reached equilibrium. This usually required about three days. The color was then titrated out a second time. This was repeated seven times. The results are shown in Tables XI and XII and figures 4 and 5.

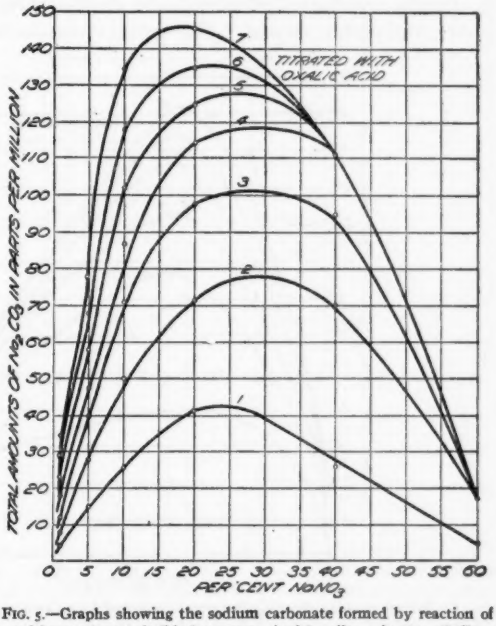

FIG. 5.—Graphs showing the sodium carbonate formed by reaction of calcium carbonate (solid phase present) with sodium nitrate. Sodium carbonate titrated out with oxalic acid, allowing equilibrium to be established between successive titrations. Numbers refer to titrations. Each graph represents the total sodium carbonate neutralized up to and including that titration.

In the reaction between sodium nitrate and calcium carbonate, sodium carbonate was formed, and this was titrated out by the acetic acid as represented by the following reaction: $Na_2CO_3+2HC_2H_3O_2 \rightleftarrows 2NaC_2H_3O_2+H_2O+CO_2$.

If under field conditions some sodium carbonate is formed by the action of sodium nitrate upon calcium carbonate and is neutralized by some weak soil acid, more sodium carbonate will be formed. This reaction will therefore continue until enough of the soluble lime salt, calcium nitrate, is formed to put an end to the reaction, as shown in Table V.

TABLE XII.—*Titrations with oxalic acid of the sodium nitrate-calcium carbonate solutions*

Solution No.	Strength of solution.	Parts per million of sodium carbonate (totals).						
		First titration.	Second titration.	Third titration.	Fourth titration.	Fifth titration.	Sixth titration.	Seventh titration.
1	Boiled water	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	1 per cent of sodium nitrate	5.3	8.0	13.3	18.6	23.9	29.2	34.5
3	5 per cent of sodium nitrate	15.9	29.1	39.7	47.6	58.2	68.8	79.4
4	10 per cent of sodium nitrate	26.5	50.3	71.5	87.4	103.3	119.2	135.1
5	20 per cent of sodium nitrate	42.4	71.6	98.1	114.0	124.6	135.2	145.8
7	40 per cent of sodium nitrate	26.5	71.5	95.3	111.2	111.2	111.2	111.2
8	60 per cent of sodium nitrate	5.3	18.5	18.5	18.5	18.5	18.5	18.5

The oxalic acid titration of the sodium carbonate formed in this reaction is represented as follows: $Na_2CO_3 + H_2C_2O_4 \rightleftarrows Na_2C_2O_4 + H_2O + CO_2$, or sodium carbonate and oxalic acid in equilibrium with sodium oxalate, water, and carbon dioxid. The sodium oxalate thus formed would react

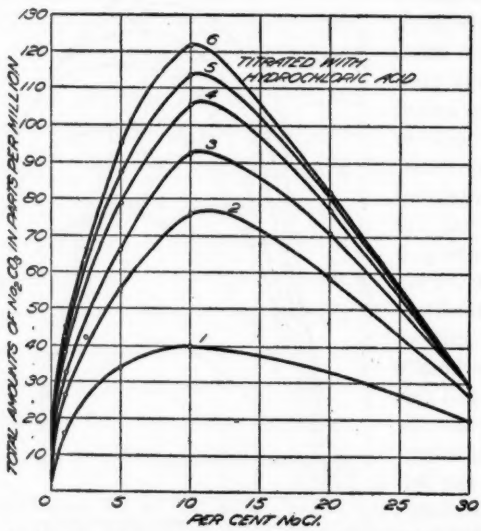

FIG. 6.—Graphs showing the sodium carbonate formed by reaction of calcium carbonate (solid phase present) and sodium chlorid. Sodium carbonate titrated out with hydrochloric acid, allowing equilibrium to be established between successive titrations. Numbers refer to titrations. Each graph represents the total sodium carbonate neutralized up to and including that titration.

with the soluble calcium nitrate produced by the first reaction and the insoluble calcium oxalate would be precipitated: $Na_2C_2O_4 + Ca(NO_3)_2 \rightleftarrows CaC_2O_4 + 2NaNO_3$.

A noticeable feature of these curves is their tendency to elongate in the meridian where the formation of sodium carbonate is most pro-

nounced. When oxalic acid is used, so that an insoluble salt of lime is formed, there is a pronounced tendency for the curves to swing toward the axis of ordinates.

The system, sodium nitrate-calcium carbonate, was then titrated out with nitric acid and the systems, sodium chlorid-calcium carbonate and

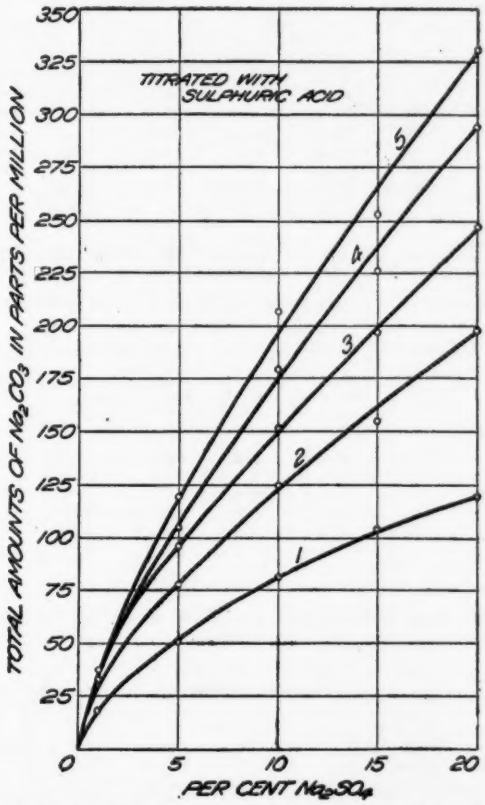

FIG. 7.—Graphs showing the sodium carbonate formed by reaction of calcium carbonate (solid phase present) and sodium sulphate. Sodium carbonate titrated out with sulphuric acid, allowing equilibrium to be established between successive titrations. Numbers refer to titrations. Each graph represents the total sodium carbonate neutralized up to and including that titration.

sodium sulphate-calcium carbonate, were titrated out in the same way with hydrochloric acid and sulphuric acid, respectively. These results are given in Tables XIII, XIV, and XV, and the curves for the hydrochloric and sulphuric acid titrations are shown on figures 6 and 7.

TABLE XIII.—*Titrations with nitric acid of the sodium nitrate-calcium carbonate solution*

Solution No.	Parts per million of sodium carbonate (totals).						
	Percentage of sodium nitrate.	1st titration.	2d titration.	3d titration.	4th titration.	5th titration.	6th titration.
1	0	0.0	0.0	0.0	0.0	0.0	0.0
2	1	10.6	23.8	31.7	37.0	44.9	52.8
3	5	39.7	94.1	92.6	105.8	118.0	128.6
4	10	66.2	111.3	132.5	145.7	158.9	165.8
5	20	60.9	94.9	121.4	137.3	145.1	153.0
6	30	34.4	68.8	84.7	95.3	103.9	106.5
7	40	34.4	58.2	74.1	79.4	79.4	79.4
8	60	23.8	37.0	37.0	37.0	37.0	37.0

TABLE XIV.—*Titrations with hydrochloric acid of the sodium chlorid-calcium carbonate solutions*

Solution No.	Parts per million of sodium carbonate (totals).						
	Percentage of sodium chlorid.	1st titration.	2d titration.	3d titration.	4th titration.	5th titration.	6th titration.
1	0	0.0	0.0	0.0	0.0	0.0	0.0
2	1	15.9	26.5	31.8	37.1	42.4	45.0
3	5	34.4	55.6	66.2	79.5	87.4	95.4
4	10	39.7	76.8	92.7	106.0	113.9	122.0
5	20	26.5	58.3	71.5	76.8	82.1	82.1
6	30	21.2	26.5	29.1	29.1	29.1	29.1

TABLE XV.—*Titrations with sulphuric acid of the sodium sulphate-calcium carbonate solutions*

Solution No.	Parts per million of sodium carbonate (totals).					
	Percentage of sodium sulphate.	1st titration.	2d titration.	3d titration.	4th titration.	5th titration.
1	0	0.0	0.0	0.0	0.0	0.0
2	1	21.2	34.4	37.0	37.0	37.0
3	5	53.0	76.8	95.3	108.5	121.7
4	10	79.5	124.5	153.6	182.7	209.2
5	15	106.0	156.3	195.7	224.8	251.6
6	20	122.0	198.8	249.1	294.1	336.5

In the soil, under field conditions, in the presence of carbon dioxid the greater part of the sodium carbonate would take up carbon dioxid and form sodium bicarbonate $Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NaHCO_3$. The three systems described above were run, and carbon dioxid in solution was used

to titrate out the phenolphthalein color. A standard solution of carbon dioxid was prepared by saturating water containing calcium carbonate in

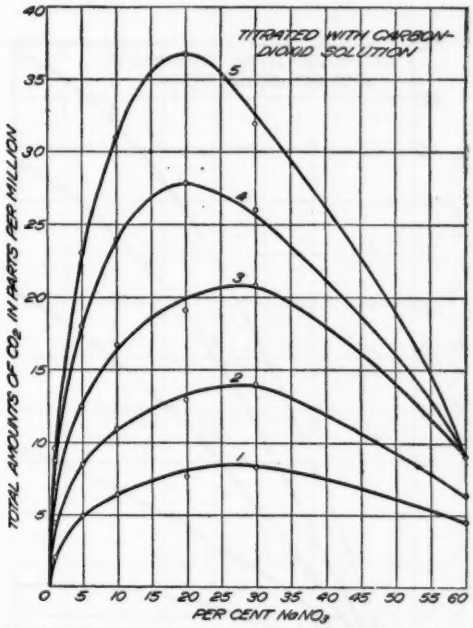
TITRATED WITH CARBON-DIOXID SOLUTION
TOTAL AMOUNTS OF CO_2 IN PARTS PER MILLION
PER CENT $NaNO_3$
0 5 10 15 20 25 30 35 40 45 50 55 60
40 35 30 25 20 15 10 5
1 2 3 4 5

FIG. 8.—Graph showing the same system as in figure 5, but titrated with carbon-dioxid solution.

excess with the carbon-dioxid gas. A fairly stable solution of calcium bicarbonate (or calcium carbonate dissolved in carbon dioxid) was ob-

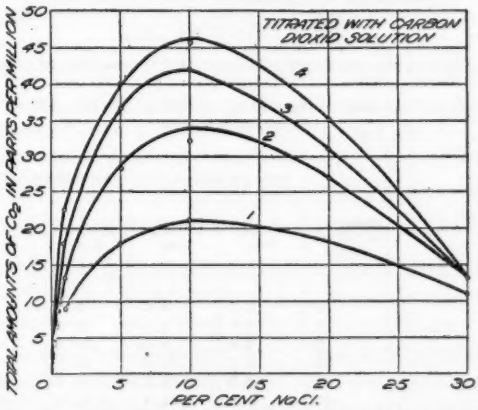
TITRATED WITH CARBON DIOXID SOLUTION
TOTAL AMOUNTS OF CO_2 IN PARTS PER MILLION
PER CENT NaCl.
0 5 10 15 20 25 30
50 45 40 35 30 25 20 15 10 5
1 2 3 4

FIG. 9.—Graph showing the same system as in figure 6, but titrated with carbon-dioxid solution.

tained and standardized to contain 360 parts per million of carbon dioxid. The results of these titrations are shown in Tables XVI, XVII,

TABLE XIII.—*Titrations with nitric acid of the sodium nitrate-calcium carbonate solution*

Solution No.	Parts per million of sodium carbonate (totals).						
	Percentage of sodium nitrate.	1st titration.	2d titration.	3d titration.	4th titration.	5th titration.	6th titration.
1	0	0.0	0.0	0.0	0.0	0.0	0.0
2	1	10.6	23.8	31.7	37.0	44.9	52.8
3	5	39.7	94.1	92.6	105.8	118.0	128.6
4	10	66.2	111.3	132.5	145.7	158.9	165.8
5	20	60.9	94.9	121.4	137.3	145.1	153.0
6	30	34.4	68.8	84.7	95.3	103.9	106.5
7	40	34.4	58.2	74.1	79.4	79.4	79.4
8	60	23.8	37.0	37.0	37.0	37.0	37.0

TABLE XIV.—*Titrations with hydrochloric acid of the sodium chlorid-calcium carbonate solutions*

Solution No.	Parts per million of sodium carbonate (totals).						
	Percentage of sodium chlorid.	1st titration.	2d titration.	3d titration.	4th titration.	5th titration.	6th titration.
1	0	0.0	0.0	0.0	0.0	0.0	0.0
2	1	15.9	26.5	31.8	37.1	42.4	45.0
3	5	34.4	55.6	66.2	79.5	87.4	95.4
4	10	39.7	76.8	92.7	106.0	113.9	122.0
5	20	26.5	58.3	71.5	76.8	82.1	82.1
6	30	21.2	26.5	29.1	29.1	29.1	29.1

TABLE XV.—*Titrations with sulphuric acid of the sodium sulphate-calcium carbonate solutions*

Solution No.	Parts per million of sodium carbonate (totals).					
	Percentage of sodium sulphate.	1st titration.	2d titration.	3d titration.	4th titration.	5th titration.
1	0	0.0	0.0	0.0	0.0	0.0
2	1	21.2	34.4	37.0	37.0	37.0
3	5	53.0	76.8	95.3	108.5	121.7
4	10	79.5	124.5	153.6	182.7	209.2
5	15	106.0	156.3	195.7	224.8	251.6
6	20	122.0	198.8	249.1	294.1	336.5

In the soil, under field conditions, in the presence of carbon dioxid the greater part of the sodium carbonate would take up carbon dioxid and form sodium bicarbonate $Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NaHCO_3$. The three systems described above were run, and carbon dioxid in solution was used

to titrate out the phenolphthalein color. A standard solution of carbon dioxid was prepared by saturating water containing calcium carbonate in

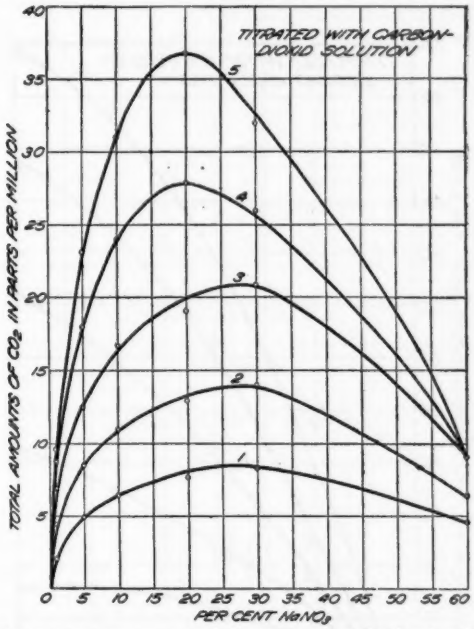

FIG. 8.—Graph showing the same system as in figure 5, but titrated with carbon-dioxid solution.

excess with the carbon-dioxid gas. A fairly stable solution of calcium bicarbonate (or calcium carbonate dissolved in carbon dioxid) was ob-

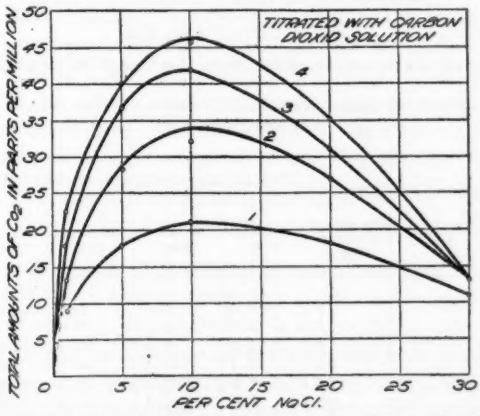

FIG. 9.—Graph showing the same system as in figure 6, but titrated with carbon-dioxid solution.

tained and standardized to contain 360 parts per million of carbon dioxid. The results of these titrations are shown in Tables XVI, XVII,

and XVIII, and figures 8, 9, and 10. The titration of the control, in which no sodium salt was present, was subtracted from each of the others.

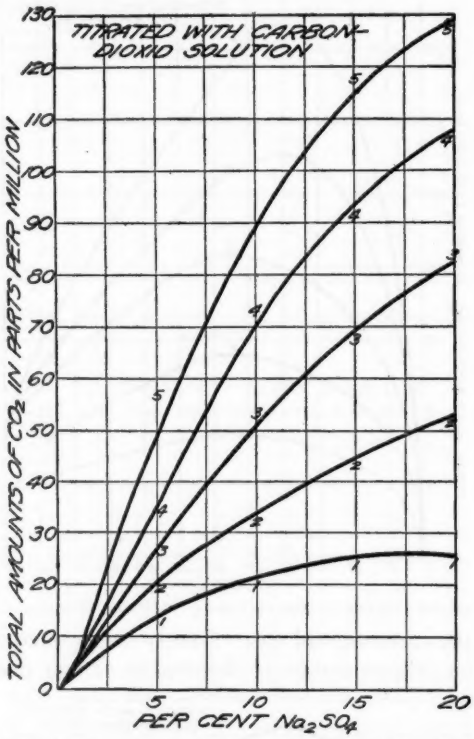

FIG. 10.—Graph showing the same system as in figure 7, but titrated with carbon-dioxid solution.

TABLE XVI.—*Titrations with carbon-dioxid solutions of the sodium nitrate-calcium carbonate solutions*

Solution No.	Parts per million of sodium carbonate (totals).					
	Percentage of sodium nitrate.	1st titration.	2d titration.	3d titration.	4th titration.	5th titration.
1	0	0.0	0.0	0.0	0.0	0.0
2	1	2.0	4.5	7.0	8.8	9.8
3	5	5.0	8.6	12.5	17.9	23.3
4	10	6.3	11.0	16.7	23.9	31.1
5	20	7.6	13.0	19.1	28.1	37.1
6	30	8.0	14.2	21.0	26.4	31.8
7	60	4.7	6.5	9.0	9.0	9.0

TABLE XVII.—*Titrations with carbon-dioxid solutions of the sodium chlorid calcium carbonate solutions*

Solution No.	Parts per million of carbon dioxid required (totals).				
	Percentage of sodium chlorid	1st titration.	2d titration.	3d titration.	4th titration.
1	0	0.0	0.0	0.0	0.0
2	1	9.0	14.4	18.7	22.3
3	5	18.0	28.8	36.7	40.3
4	10	21.6	32.4	42.1	46.1
5	20	18.0	27.0	31.3	35.3
6	30	10.8	12.6	12.6	12.6

TABLE XVIII.—*Titrations with carbon-dioxid solutions of the sodium sulphate calcium carbonate solutions*

Solution No.	Parts per million of carbon dioxid required (totals).					
	Percentage of sodium sulphate.	1st titration.	2d titration.	3d titration	4th titration.	5th titration.
1	0	0.0	0.0	0.0	0.0	0.0
2	1	3.6	5.0	3.9	3.9	3.9
3	5	14.4	21.6	27.7	34.9	55.5
4	10	19.8	34.2	54.7	74.5	88.9
5	15	23.4	42.6	66.7	91.1	117.1
6	20	25.2	54.0	81.7	106.9	128.5

By considering the curves, one after another, a very definite idea is obtained of what might happen in the soil when a minimum amount of carbon dioxid is present and being generated continuously. The sodium salts, acting upon the calcium carbonate, would form a small amount of sodium carbonate, and this would combine with the carbon dioxid being generated in the soil and form sodium bicarbonate. Equilibrium would be upset and more sodium carbonate would be formed, which in its turn would be converted into sodium bicarbonate, and the reactions would continue until equilibrium was established. Equilibrium would depend upon the amount of the soluble lime salt formed in the reaction.

EQUILIBRIUM UNDER SOIL CONDITIONS

Cameron and Seidell, in studying the reaction of sodium chlorid and sodium sulphate with calcium carbonate, drew air through the solutions until equilibrium was established with atmospheric air. In applying their results to soil conditions one is apt to fall into error, for soil air contains a great deal more carbon dioxid than atmospheric air. Carbon dioxid will hold calcium carbonate in solution in a fairly stable form until an inert gas is bubbled through the solution. This bubbling process will effectually wash out the carbon dioxid and precipitate the salt. In the

the same way the equilibrium between carbonates and bicarbonates can be changed by modifying the partial pressure of the carbon dioxid in the gas phase. In a study of soil solutions a system whose stability is dependent upon the gas phase is often of more importance than one consisting wholly of stable salts. Equilibrium conditions are, furthermore, not necessarily reached in any soil solution. The movement of the soil moisture may remove the salt which is formed in one place and carry it to another in a rather unstable condition

The presence of the carbon dioxid in the atmospheric air is due in large part to the action of the bacteria and other organisms upon the organic matter of the soil. If a soil solution containing sodium chlorid, for example, be in contact with the solid calcium carbonate and the bacteria begin to generate carbon dioxid, the gas will appear and pass through the soil solution in its way through the soil toward the outside air. In other words, the equilibrium between sodium chlorid and calcium carbonate, so far as soil conditions are concerned, may be determined by a much higher partial pressure of carbon dioxid than is present in atmospheric air.

REACTION BETWEEN SODIUM SALTS AND CALCIUM CARBONATE IN PRESENCE OF CARBON DIOXID AT ATMOSPHERIC PRESSURE

Solutions of sodium salts with the solid calcium carbonate were prepared as before described and brought to equilibrium with carbon dioxid. This was accomplished by passing carbon dioxid into the solutions until the gas that was readily absorbed had been taken up. The shaker bottles (1-quart milk bottles), which were about half full of the solutions, were then filled with carbon dioxid, tightly stoppered, and shaken until final equilibrium was reached. This filling of the bottle with carbon dioxid and shaking it had to be repeated a great many times and over a period of several days. The final product represented equilibrium between the sodium salt and calcium carbonate in an atmosphere approaching pure carbon dioxid. Portions of the solution were withdrawn and titrations made with standard sulphuric acid. The titration figure of No. 1, in which

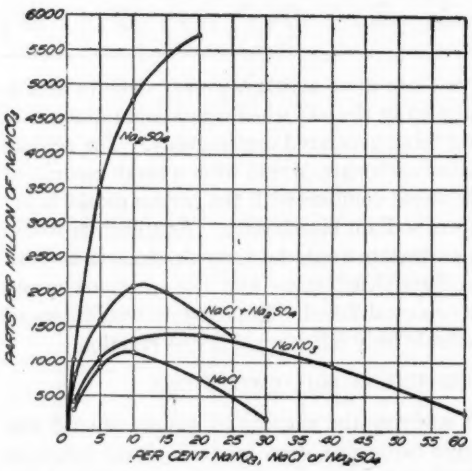

FIG. 11.—Graphs showing the concentration of sodium bicarbonate in the systems discussed above when in equilibrium with carbon dioxid at approximately atmospheric pressure.

there was no sodium salt, was subtracted from each of the other readings, and the results calculated to sodium bicarbonate. As methyl orange is not sensitive in a concentrated solution of some of the sodium salts, the titrations were made by adding an excess of the standard acid, boiling off the liberated carbon dioxid, and titrating back the excess with standard sodium hydrate, using phenolphthalein as an indicator. Tables XIX, XX, XXI, and XXII, and figure 11 show the amount of sodium bicarbonate formed in the presence of carbon dioxid.

After all the determinations had been made and duplicated, an excess of calcium sulphate was added to the solutions and they were again shaken until they had reached equilibrium. This action of the sodium salts upon calcium carbonate in the presence of gypsum is also shown in the above-mentioned tables and in figure 12.

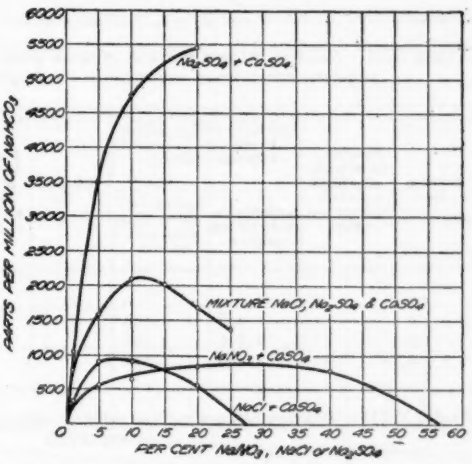

FIG. 12. Graph showing the same systems as in figure 11, with the addition of calcium sulphate in excess.

In short, a system consisting of calcium carbonate in excess carbon dioxid at atmospheric pressure, and one or more of the three salts sodium chlorid, sodium nitrate, or sodium sulphate, may react to form very appreciable quantities of sodium bicarbonate. The maximum amount of sodium bicarbonate formed in each system was as follows: With sodium nitrate, 1,386 parts per million; with sodium chlorid, 1,155 parts per million; with sodium sulphate, 5,712 parts per million; with equal parts of sodium chorid and sodium sulphate 2,100 parts per million.

TABLE XIX.—*Reaction between sodium nitrate and calcium carbonate in the presence of carbon dioxid*

Solution No.	Percentage of sodium nitrate.	Parts per million of sodium bicarbonate formed with—		Solution No.	Percentage of sodium nitrate.	Parts per million of sodium bicarbonate formed with—	
		Sodium nitrate.	Sodium nitrate+ calcium sulphate.			Sodium nitrate.	Sodium nitrate+ calcium sulphate.
1	0	0	0	5	20	1,386	840
2	1	462	336	6	40	966	798
3	5	1,050	546	7	60	252	0
4	10	1,302	672				

TABLE XX.—*Reaction between sodium chlorid and calcium carbonate in the presence of carbon dioxid*

Solution No.	Percentage of sodium chlorid.	Parts per million of sodium bicarbonate formed with—		Solution No.	Percentage of sodium chlorid.	Parts per million of sodium bicarbonate formed with—	
		Sodium chlorid.	Sodium chlorid + calcium sulphate.			Sodium chlorid.	Sodium chlorid + calcium sulphate.
1	0	0	0	4	10	1,155	924
2	1	357	353	5	20	735	546
3	5	987	924	6	30	147	0

TABLE XXI.—*Reaction between mixtures of equal parts of sodium chlorid and sodium sulphate, and calcium carbonate in the presence of carbon dioxid*

Solution No.	Percentage in mixture of sodium chlorid + sodium sulphate.	Parts per million sodium bicarbonate formed with equal parts of—		Solution No.	Percentage in mixture of sodium chlorid + sodium sulphate.	Parts per million sodium bicarbonate formed with equal parts of—	
		Sodium chlorid + sodium sulphate.	Sodium chlorid + sodium sulphate + calcium.			Sodium chlorid + sodium sulphate.	Sodium chlorid + sodium sulphate + calcium.
1	0	0	0	5	15	2,016	2,016
2	1	798	798	6	20	1,680	1,680
3	5	1,596	1,596	7	25	1,386	1,386
4	10	2,100	2,100				

TABLE XXII.—*Reaction between sodium sulphate and calcium carbonate in the presence of carbon dioxid*

Solution No.	Percentage of sodium sulphate.	Parts per million sodium bicarbonate formed with—		Solution No.	Percentage of sodium sulphate.	Parts per million sodium bicarbonate formed with—	
		Sodium sulphate alone.	Sodium sulphate + calcium sulphate.			Sodium sulphate alone.	Sodium sulphate + calcium sulphate.
1	0	0	0	4	10	4,788	4,788
2	1	1,008	1,008	5	20	5,712	5,712
3	5	3,528	3,528				

THEORETICAL EFFECT OF A FIELD APPLICATION OF GYPSUM ON BLACK ALKALI

It was long ago suggested by Dr. Hilgard that an application of gypsum would improve soils containing black alkali. This method of reclaiming alkali soils has been used a great many times, with and without success. By reference to the foregoing tables and graphs, one can form a definite idea of what will happen when gypsum is applied to any par-

ticular type of alkali. It will be noted that the presence of calcium sulphate materially affected the reaction in the case of sodium nitrate and sodium chlorid; but, as might be expected, no effect was in evidence in the case of sodium sulphate or the mixture containing sodium sulphate, since in the reaction of sodium sulphate and calcium carbonate gypsum (calcium sulphate) is one of the salts formed. Aside from the effect of lime in the rôle of an antagonistic agent, which will be discussed later, one would predict from these results that an application of gypsum would have little or no effect in overcoming black alkali that is being formed by the action of sodium sulphate or mixtures of alkali containing sodium sulphate upon lime. Furthermore, as many irrigation waters already contain gypsum in appreciable amounts, little or no beneficial effect may be expected from an application of gypsum to soils irrigated with such waters.

EFFECT OF SOLUBLE LIME SALTS UPON THE FORMATION OF SODIUM BICARBONATE

As has been pointed out before, equilibrium must not necessarily be reached in any of these reactions before the resulting components are

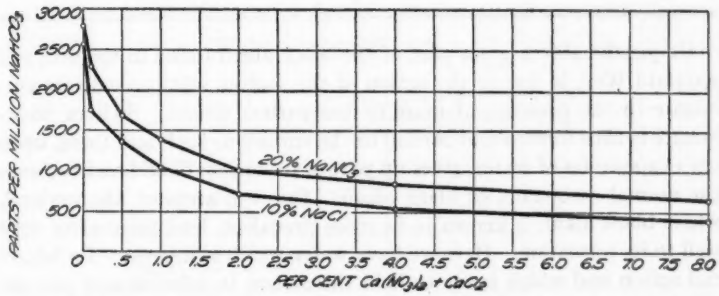

FIG. 13.—Graphs showing the effect of soluble calcium salts upon the formation of sodium bicarbonate.

carried away by drainage or the capillary action of the water. However, in case the soluble lime remained in the place where it was formed, the reaction would, of course, grow less with the increasing concentration of lime. In order to determine the effect of these soluble lime salts on the formation of sodium bicarbonate, solutions containing graduated amounts of calcium nitrate in 20 per cent solutions of sodium nitrate, and graduated amounts of calcium chlorid in 10 per cent solutions of sodium chlorid were prepared and brought to equilibrium by bubbling carbon-dioxid gas through them. These results are shown in Tables XXIII and XXIV and in figure 13.

TABLE XXIII.—*Reaction between 20 per cent solutions of sodium nitrate and calcium carbonate in the presence of calcium nitrate and carbon dioxid at atmospheric pressure*

Solution No.	Percentage of calcium nitrate.	Parts per million of sodium bicarbonate formed.	Solution No.	Percentage of calcium nitrate.	Parts per million of sodium bicarbonate formed.
1	0.0	2,814	5	2.0	1,008
2	.1	2,268	6	4.0	898
3	.5	1,680	7	8.0	672
4	1.0	1,428			

TABLE XXIV.—*Reaction between 10 per cent solutions of sodium chlorid and calcium carbonate in the presence of calcium chlorid and carbon dioxid at atmospheric pressure*

Solution No.	Percentage of calcium chlorid.	Parts per million of sodium bicarbonate formed.	Solution No.	Percentage of calcium chlorid.	Parts per million of sodium bicarbonate formed.
1	0.0	2,562	5	2.0	731
2	.1	1,764	6	4.0	563
3	.5	1,386	7	8.0	420
4	1.0	1,067			

Unquestionably a great part of the black alkali found in the arid and semiarid West is due to the action of the sodium salts on calcium carbonate in the presence of more or less carbon dioxid. Sodium bicarbonate is thus formed and carried to the surface as such and there, upon the evaporation of water, gives up part of its carbon dioxid and becomes the normal carbonate, or black alkali. The wet areas of the lowland, where black alkali is known to be more prevalent, lend themselves very well to its formation. Here we have water which is necessary for bacterial action and which tends to hold the carbon in solution and prevent its rapid escape into the atmosphere.

In the consideration of black alkali its formation under field conditions in a practically saturated solution of the sodium salt is not an overdrawn conception. When the sodium salt exists in any appreciable quantity in a soil it will at some time or other, by alternate dilution and evaporation, exist in all the different concentrations, from a dilute solution up to the salt crystal itself. This will happen in a soil that is irrigated regularly, saturated with water, and then allowed to dry down to near the wilting point between irrigations.

EXPERIMENTS WITH SAND AND SOIL

A large sample of soil was taken from the grounds of the new Citrus Experiment Station at Riverside, California, sifted through a 2 mm. sieve, mixed and dried in the sun for analysis. This soil, when shaken

up with distilled water and allowed to come to equilibrium, gave an extract that would show color with phenolphthalein upon boiling. This soil, however, would not visibly effervesce with dilute acid. It contained

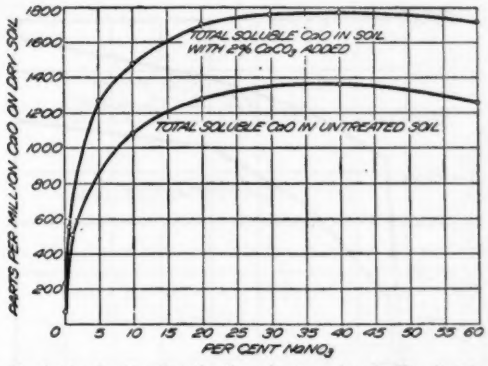

FIG. 14.—Graphs showing the effect of sodium nitrate on the solubility of calcium in soil.

just enough calcium carbonate or soluble silicates to make it basic in character. It contained 0.30 per cent of total calcium oxid on digestion with strong hydrochloric acid (specific gravity 1.115) and 0.83 per cent of humus. Part of the soil was taken and 2 per cent of its weight of

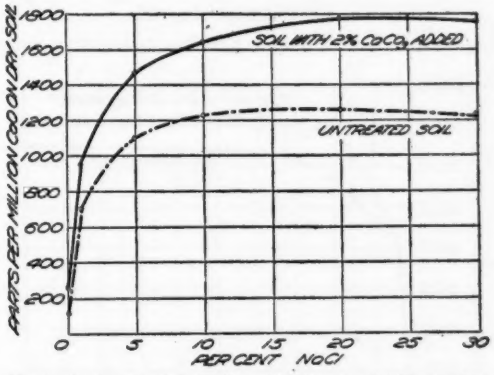

FIG. 15.—Graphs showing the effect of sodium chlorid on the solubility of calcium in soil.

calcium carbonate added and mixed with it. Portions of the original soil and also the soil to which the calcium carbonate had been added were shaken up with graduated solutions of each of the three salts sodium nitrate, sodium chlorid, and sodium sulphate and mixtures of

equal parts of sodium chlorid and sodium sulphate, in the proportion of 1 of soil to 5 of the solution and brought to equilibrium. The solutions were then filtered and analyzed for calcium oxid.

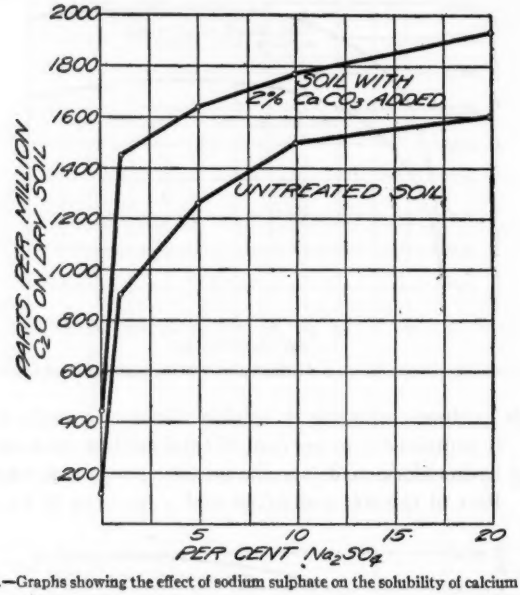

FIG. 16.—Graphs showing the effect of sodium sulphate on the solubility of calcium in soil.

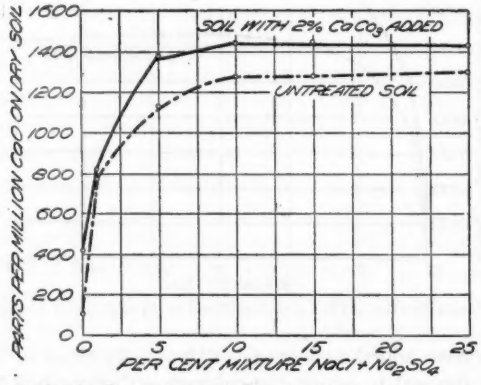

FIG. 17.—Graphs showing the effect of mixtures of sodium chlorid and sodium sulphate on the solubility of calcium in soil.

The amounts of lime, calculated to calcium oxid soluble in the different salts, are shown in Tables XXV, XXVI, XXVII, and XXVIII and are brought together in figures 14, 15, 16, and 17.

TABLE XXV.—*Solubility of lime in solutions of sodium nitrate*

Solution No.	Percentage of sodium nitrate.	Parts per million of soluble calcium oxid on basis of dry soil in—		Solution No.	Percentage of sodium nitrate.	Parts per million of soluble calcium oxid on basis of dry soil in—	
		Untreated soil.	Soil+2 per cent of calcium carbonate.			Untreated soil.	Soil+2 per cent of calcium carbonate.
1	0	70	230	5	20	1,280	1,708
2	1	533	558	6	30	.....	1,759
3	5	1,005	1,284	7	40	1,359	1,780
4	10	1,079	1,484	8	60	1,275	1,723

TABLE XXVI.—*Solubility of lime in solutions of sodium chlorid*

Solution No.	Percentage of sodium chlorid.	Parts per million of soluble calcium oxid on basis of dry soil in—		Solution No.	Percentage of sodium chlorid.	Parts per million of soluble calcium oxid on basis of dry soil in—	
		Untreated soil.	Soil+2 per cent of calcium carbonate.			Untreated soil.	Soil+2 per cent of calcium carbonate.
1	0	105	273	4	10	1,239	1,638
2	1	714	942	5	20	1,258	1,783
3	5	1,113	1,470	6	30	1,239	1,764

TABLE XXVII.—*Solubility of lime in solutions of sodium sulphate*

Solution No.	Percentage of sodium sulphate.	Parts per million of soluble calcium oxid on basis of dry soil in—		Solution No.	Percentage of sodium sulphate.	Parts per million of soluble calcium oxid on basis of dry soil in—	
		Untreated soil.	Soil+2 per cent of calcium carbonate.			Untreated soil.	Soil+2 per cent of calcium carbonate.
1	0	125	420	4	10	1,490	1,785
2	1	905	1,450	5	20	1,600	1,935
3	5	1,260	1,635				

TABLE XXVIII.—*Solubility of lime in solutions of mixtures of sodium chlorid and sodium sulphate*

Solution No.	Percentage of mixture (sodium chlorid+sodium sulphate).	Parts per million of soluble calcium oxid on basis of dry soil in—		Solution No.	Percentage of mixture (sodium chlorid+sodium sulphate).	Parts per million of soluble calcium oxid on basis of dry soil in—	
		Untreated soil.	Soil+2 per cent of calcium carbonate.			Untreated soil.	Soil+2 per cent of calcium carbonate.
1	0	125	420	4	10	1,278	1,438
2	1	780	815	5	15	1,285	1,445
3	5	1,155	1,395	6	25	1,300	1,430

REACTION BETWEEN SODIUM SALTS AND CALCIUM CARBONATE IN THE SOIL

By reference to the tables it will be noticed in every case that considerably more lime went into solutions in the soils to which calcium carbonate had been added than in the untreated soils. With the sodium nitrate, Table XXV, this difference amounted to 448 parts per million; with sodium chlorid, Table XXVI, to 525 parts per million; with sodium sulphate, Table XXVII, to 335 parts per million; and with a mixture of sodium chlorid and sodium sulphate, Table XXVIII, to 130 parts per million at the maximum concentration. The increase in the soluble lime can be accounted for by the action of the sodium salts upon calcium carbonate and the formation of the normal carbonate, or black alkali, and the subsequent formation of sodium bicarbonate—for example, $Na_2SO_4 + CaCO_3 \rightleftarrows Na_2CO_3 + CaSO_4$. With the development of car-

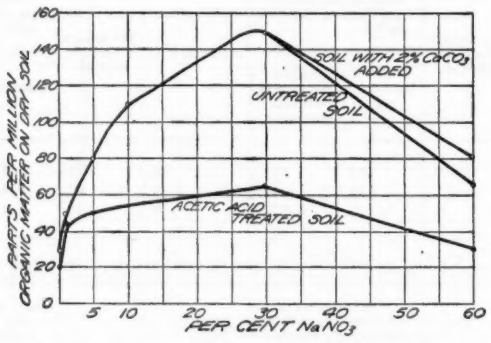

FIG. 18.—Graphs showing the solubility of organic matter in soil in solutions of sodium nitrate.

bon dioxid in the solution the normal carbonate was converted into bicarbonate; however, at one time in the reaction, sodium carbonate existed, and when in this condition it was capable of reacting and did react upon the organic matter and the silica of the soil. It was noticed that the color of the solutions, owing to soluble organic matter, increased in intensity as the strength of the sodium salt increased, showing the action of the sodium carbonate formed in the reaction upon the organic matter.

ACTION OF SODIUM CARBONATE UPON ORGANIC MATTER IN THE SOIL

In order to have a soil which contained no carbonates, a quantity of the Station soil was mixed with dilute acetic acid until the soil extract was distinctly acid. This required about 4 c. c. of normal acetic acid to every 100 gm. of soil. After being thoroughly mixed, the soil was allowed to dry in the sun and the excess of acetic acid driven off in this way.

Portions of acid-treated soil, untreated soil, and soil to which 2 per cent of calcium carbonate had been added were then separately shaken up with the sodium salts in the usual way. When equilibrium was established, the solutions were filtered off and the soluble organic matter was determined by colorimeter readings against a known standard prepared from peat by extracting the organic matter with ammonia. These results are shown in Tables XXIX, XXX, XXXI, and XXXII and in figures 18, 19, 20, and 21.

TABLE XXIX.—*Solubility of organic matter in solutions of sodium nitrate*

Solution No.	Percentage of sodium nitrate.	Parts per million of soluble organic matter.			Solution No.	Percentage of sodium nitrate.	Parts per million of soluble organic matter.		
		Untreated soil.	Soil+2 per cent of calcium carbonate.	Acetic-acid-treated soil.			Untreated soil.	Soil+2 per cent of calcium carbonate.	Acetic-acid-treated soil.
1	0	30	30	20	4	10	110	110	55
2	1	50	50	45	5	30	150	150	65
3	5	80	80	50	6	60	65	80	30

TABLE XXX.—*Solubility of organic matter in solutions of sodium chlorid*

Solution No.	Percentage of sodium chlorid.	Parts per million of soluble organic matter.			Solution No.	Percentage of sodium chlorid.	Parts per million of soluble organic matter.		
		Untreated soil.	Soil+2 per cent of calcium carbonate.	Acetic-acid-treated soil.			Untreated soil.	Soil+2 per cent of calcium carbonate.	Acetic-acid-treated soil.
1	0	30	30	15	4	10	60	60	30
2	1	45	45	35	5	20	50	50	30
3	5	60	60	35	6	30	30	30	30

TABLE XXXI.—*Solubility of organic matter in solutions of sodium sulphate*

Solution No.	Percentage of sodium sulphate.	Parts per million of soluble organic matter.			Solution No.	Percentage of sodium sulphate.	Parts per million of soluble organic matter.		
		Untreated soil.	Soil+2 per cent of calcium carbonate.	Acetic-acid-treated soil.			Untreated soil.	Soil+2 per cent of calcium carbonate.	Acetic-acid-treated soil.
1	0	30	30	20	4	10	420	440	190
2	1	110	110	60	5	20	460	500	200
3	5	300	300	130					

TABLE XXXII.—*Solubility of organic matter in solutions of mixtures of sodium chlorid and sodium sulphate*

Solution No.	Percentage of mixture (sodium chlorid+sodium sulphate).	Parts per million of soluble organic matter.			Solution No.	Percentage of mixture (sodium chlorid+sodium sulphate).	Parts per million of soluble organic matter.		
		Untreated soil.	Soil+2 per cent of calcium carbonate.	Acetic-acid-treated soil.			Untreated soil.	Soil+2 per cent of calcium carbonate.	Acetic acid-treated soil.
1	0	30	30	15	4	10	190	190	90
2	1	75	75	45	5	15	190	190	.....
3	5	150	150	80	6	25	175	175	70

It will be seen by reference to the graphs that the curves for the untreated soil follow very closely the curves of the soil to which 2 per cent of calcium carbonate had been added. This seems to indicate that,

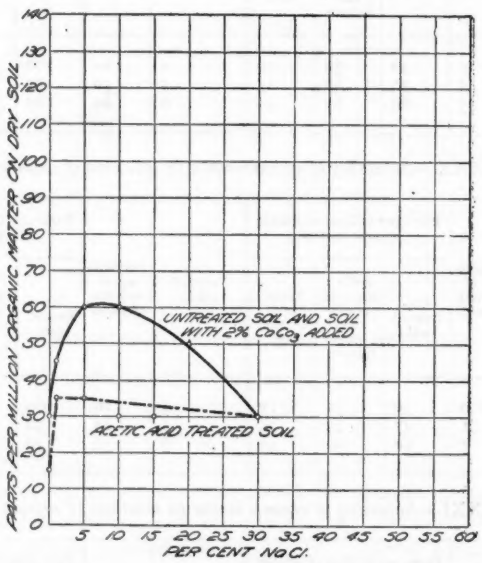

FIG. 19.—Graphs showing the solubility of organic matter in soil in solutions of sodium chlorid.

although there was not enough calcium carbonate in the untreated soil to visibly effervesce with acid, still there was enough to react with the sodium salts and to form sodium carbonate until equilibrium was reached, and to all purposes it was a calcareous soil. The difference in the solubility of the organic matter in the acid-treated soil and the lime or untreated soil is a fair measure of the action of the sodium salts upon calcium carbonate with the formation of sodium carbonate.

It seems from these results as if the normal carbonate was being formed, although it was impossible to detect it by phenolphthalein, except in one

instance, with the highest concentration of sodium sulphate. The sodium appeared, however, in the titrations as bicarbonate. The first chemical change seemed to be the formation of the normal carbonate,

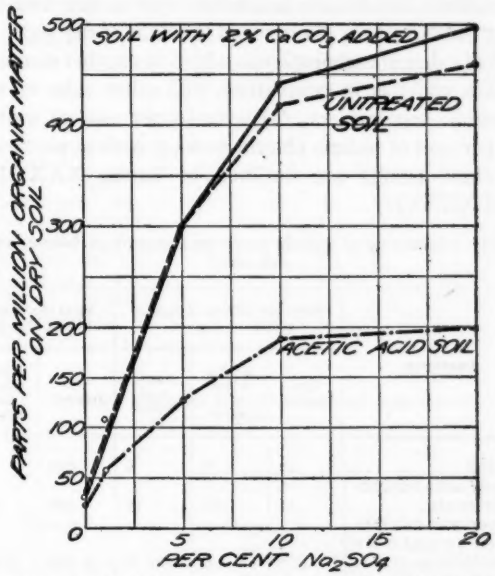

FIG. 20.—Graphs showing the solubility of organic matter in soil in solutions of sodium sulphate.

and while in this condition (the "nascent," or transition state, so to speak, between the carbonate and bicarbonate) it reacted with the organic matter and silica of the soil. Practically speaking, it was at

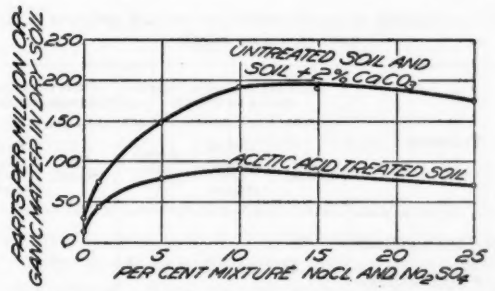

FIG. 21.—Graphs showing the solubility of organic matter in soil in presence of mixtures of sodium chlorid and sodium sulphate.

this stage in a "nascent" state, and seemed to possess some of the properties of a "nascent" element.

To test this point, a sample of soil was washed with dilute hydrochloric acid until the lime was all washed out. The soil was then washed

with water until free from hydrochloric acid, and was dried in the sun. Samples of the untreated, hydrochloric-acid-treated, and acetic-acid-treated soil were treated as outlined in the following tables. A saturated solution of calcium bicarbonate in solution with carbon dioxid was added to the soil at the rate of 0.4 per cent, on the basis of dry soil. An equivalent amount of calcium carbonate was added to another sample, and these were run with controls in comparison with other salts of calcium: (1) With no sodium salt present, (2) with 10 per cent of sodium nitrate, (3) with 10 per cent of sodium chlorid, and (4) with 10 per cent of sodium sulphate. These results are outlined in Tables XXXIII, XXXIV, XXXV, and XXXVI.

TABLE XXXIII.—*Solubility of organic matter and calcium carbonate, with no sodium salt added*

Solution No.	Treatment.	Parts per million of organic matter on dry soil.			Parts per million of calcium carbonate calculated from HCO_3.		
		Untreated.	Hydrochloric-acid treated.	Acetic-acid treated.	Untreated.	Hydrochloric-acid treated.	Acetic-acid treated.
1	Control	22	6	6	150	0	0
2	0.4 per cent calcium carbonate	22	22	16	500	350	575
3	0.4 per cent calcium carbonate as $Ca(HCO_3)_2$	18	6	6	3,500	3,200	3,125
4	10 per cent calcium nitrate	24	6	6	.....	.....	.....
5	10 per cent calcium chlorid	22	6	6	.....	.....	.....
6	Saturated calcium sulphate	18	6	6	.....	.....	.....

TABLE XXXIV.—*Solubility of organic matter and calcium carbonate in 10 per cent solutions of sodium nitrate*

Solution No.	Treatment.	Parts per million of organic matter on dry soil.			Parts per million of calcium carbonate calculated from HCO_3.		
		Untreated.	Hydrochloric-acid treated.	Acetic-acid treated.	Untreated.	Hydrochloric-acid treated.	Acetic-acid treated.
1	10 per cent sodium nitrate	52	6	12	75	0	0
2	10 per cent sodium nitrate +0.4 per cent of calcium carbonate	70	40	40	575	700	650
3	10 per cent sodium nitrate+0.4 per cent of calcium carbonate as $Ca(HCO_3)_2$	36	20	18	3,500	2,875	3,000

TABLE XXXV.—*Solubility of organic matter and calcium carbonate in 10 per cent solutions of sodium chlorid*

Solution No.	Treatment.	Parts per million of organic matter on dry soil.			Parts per million of calcium carbonate calculated from HCO_3.		
		Untreated.	Hydrochloric-acid treated.	Acetic-acid treated.	Untreated.	Hydrochloric-acid treated.	Acetic-acid treated.
1	10 per cent sodium chlorid.....	36	6	18	100	0	0
2	10 per cent sodium chlorid+0.4 per cent of calcium carbonate.....	40	36	30	850	500	600
3	10 per cent sodium chlorid+0.4 per cent of calcium carbonate as $Ca(HCO_3)_2$.....	24	20	18	3,625	2,875	3,000

TABLE XXXVI.—*Solubility of organic matter and calcium carbonate in 10 per cent solutions of sodium sulphate*

Solution No.	Treatment.	Parts per million of organic matter on dry soil.			Parts per million of calcium carbonate calculated from HCO_3.		
		Untreated.	Hydrochloric-acid treated.	Acetic-acid treated.	Untreated.	Hydrochloric-acid treated.	Acetic-acid treated.
1	10 per cent sodium sulphate+0.4 per cent of calcium carbonate.....	176	20	140	100	0	0
2	10 per cent sodium sulphate+0.4 per cent of calcium carbonate.....	208	120	250	1,000	875	1,125
3	10 per cent sodium sulphate+0.4 per cent of calcium carbonate as $Ca(HCO_3)_2$.....	104	40	150	3,250	2,625	2,875

As will be seen from Tables XXXIII to XXXVI, with the untreated soil little difference is shown, so far as the action on the organic matter is concerned, between calcium carbonate and other calcium salts when no sodium was added. With the hydrochloric-acid and acetic-acid-treated soils the amount of organic matter fell when the other salts of calcium were present, but rose to practically the same as the untreated soil when calcium carbonate was added. Calcium nitrate, calcium chlorid, and calcium sulphate do not alone seem to affect materially the solubility of the organic matter of the soil. The acid condition of the soil,

brought about by hydrochloric and acetic acids, decidedly decreased the solubility of the organic matter.

With solutions of sodium nitrate, sodium chlorid, and sodium sulphate the solubility of the organic matter is decidedly increased by the presence of calcium carbonate. The sodium salts, however, as shown in other work, have a solvent effect upon the organic matter aside from their action upon the calcium carbonate. This is particularly true of sodium sulphate.

The tables bring out one thing quite forcibly—the probable reaction of the sodium salts with calcium carbonate in the presence of the soil with the formation of normal sodium carbonate. In the cases where the lime was added as a bicarbonate, little or no reaction was noticed above the controls. In fact, the presence of calcium bicarbonate, as shown by experiments not included in this paper, tends to protect the organic matter rather than to bring it into solution. The action of the sodium salt on the calcium bicarbonate would result in the formation of sodium bicarbonate, which is much less active in the decomposition of organic matter. This will be brought out later.

The methyl-orange titration or the titration for bicarbonates (HCO_3) was made and for convenience calculated to calcium carbonate. This is also shown in the tables. The figures represent the amount of calcium carbonate that was brought into solution in the different treatments. In the case of calcium bicarbonate the figures remain fairly constant throughout the series. With the calcium carbonate, however, a distinct increase was noticed when the sodium salts were introduced, indicating to what extent the calcium carbonate had reacted with the sodium salts, with the formation of sodium carbonate.

ACTION OF CALCIUM CARBONATE UPON ORGANIC MATTER IN THE SOIL

There is a belief prevalent in some sections that calcium acts as a protective agent upon the organic matter of the soil. This is probably due to the repeated statement of Dr. Hilgard (6, p. 283, 380–381) that lime carbonate is the principal factor in the formation of humus. Lyon and Fippin (7, p. 127) state that—

> The loss of humus by leaching from soils rich in lime is very much less than in those soils poor in lime.

This is probably true, but the comparisons were no doubt made between a fertile limestone soil and a low-lying swamp or acid peat bog, and not between a limestone soil and an acid upland soil, in which the presence of a real acid is questionable, or an upland soil deficient in lime. It is unquestionably true that lime will precipitate many organic compounds, but it is yet to be shown that a given amount of humus will be retained in the soil longer in the presence of lime than in

the absence of it. It is the writer's opinion that calcium carbonate in itself has a tendency to bring the organic matter of the soil into solution, and this action is hastened by the presence of all the sodium salts. It is true that our limestone soils are our most fertile soils, and certainly contain the most organic matter, but this is probably brought about by the fact that the vast majority of humus-forming plants thrive best upon limestone soils. An upland acid soil usually supports but a sparse vegetation, and consequently accumulates little humus. The limestone or calcium carbonate unquestionably stimulates the activity of the bacterial flora, and in this way, if in no other, would tend to destroy the organic matter of the soil. The calcareous soils, then, probably are richer in humus, not because of the protective action of lime, but because of the greater supply of organic material.

When the Citrus soils of southern California are given plenty of water, the percentage of organic matter is without doubt a great factor in productivity. These soils are usually extremely low in organic matter, and a little variation one way or the other, brought about by proper or improper cultural methods, sometimes shows very striking results.

A series of pots were filled with the soil from the new Citrus station site and treated as follows:

1. Soil untreated.
2. Soil treated with 2 per cent of calcium carbonate.
3. Soil treated with 1 per cent of manure.
4. Soil treated with 1 per cent of manure +2 per cent of calcium carbonate.
5. Soil treated with 1 per cent of ground alfalfa.
6. Soil treated with 1 per cent of ground alfalfa+2 per cent of calcium carbonate.
7. Soil treated with 1 per cent of ground melilotus.
8. Soil treated with 1 per cent of ground melilotus+2 per cent of calcium carbonate.
9. Soil treated with 1 per cent of peat (leaf mold).
10. Soil treated with 1 per cent of peat +2 per cent of calcium carbonate.

Five other soils were collected from Corona and treated with 1 per cent of alfalfa, with and without lime. All of these pots were kept moist and allowed to stand approximately for one year before being planted to lemon seedlings. In every case a depressing effect was noticed when lime was added to the soil. Four representative 5-month-old plants are shown in Plate 62, A.

The effect of lime is not noticeable when the seedlings are planted immediately after the treatment and grown for several months. As organic matter is, under the conditions of culture, the controlling factor, it seems highly probable that the depressing action of lime upon the seedlings is due to its indirect action upon the organic matter of the soil. Even in the control soil, to which no organic matter was added, the lime seems to have attacked the little organic matter existing there and, in the common term, "burned it out."

The soil from the new Citrus station has been cultivated very little and therefore retains much of its original organic matter. It is higher in that respect than the average of the soils from the much cultivated Citrus groves in the vicinity. When planted to Citrus seedlings in pots it produced much better plants than the neighboring soils, at least during the period that these plants have been under observation. This is quite likely due to the higher percentage of active organic matter in the soil and would tend to explain the fact that young Citrus groves when planted on virgin soil usually grow well at first and show little mottling until they have reached an age of 8 years or more. By this time under the system of intensive cultivation now in common practice, the active organic matter is necessarily reduced to a minimum.

Four samples of hydrochloric-acid-treated soil were washed and placed in pieces of apparatus resembling lantern chimneys, and set in shallow reservoirs. They were given the treatments outlined in Table XXXVII. Distilled water and 20 per cent solutions of sodium nitrate were placed in the reservoirs beneath and allowed to pass up through the soil and evaporate on the surface. After four days the surface crust was scraped off and the amount of organic matter brought into solution was determined.

TABLE XXXVII.—*Solubility of organic matter of black alkali soil treated with sodium-nitrate solutions*

Solution No.	Soil treatment.	Solution used in reservoirs.	Parts per million of water-soluble organic matter on dry crust.
1	2 per cent of calcium carbonate	Distilled water	0
2	None	20 per cent of sodium nitrate	116
3	.....do	20 per cent of sodium nitrate with excess calcium carbonate.	150
4	2 per cent of calcium carbonate	20 per cent of sodium nitrate	690

1. Under the conditions of this experiment, when the soil contained calcium carbonate and was treated with distilled water, little or no organic matter was brought into solution.

2. When the soil contained no carbonates and was treated with a sodium-nitrate solution, a moderate amount of organic matter was dissolved, representing the solubility of the organic matter of the soil in sodium nitrate.

3. When sodium nitrate and calcium carbonate were brought together in the reservoir, the reaction with the formation of sodium carbonate took

place outside the soil. The sodium carbonate was changed into sodium bicarbonate, and the action of the bicarbonate upon the organic matter of the soil was only a little more than that of sodium nitrate alone.

4. When calcium carbonate was mixed with the soil and the sodium-nitrate solution introduced into it, the reaction which involved the formation of the sodium carbonate took place in contact with the soil. The action of the sodium carbonate upon the organic matter is clearly brought out.

Another sample of acetic-acid-treated soil was taken, treated, first with sodium sulphate, second with sodium sulphate and calcium carbonate, and third with sodium sulphate and calcium carbonate and then the solution saturated with carbon-dioxid gas. These were shaken until equilibrium was established. Determinations were then made of the soluble organic matter (Table XXXVIII).

TABLE XXXVIII.—*Solubility of the organic matter in acetic-acid-treated soil with the addition of salts*

Solution No.	Treatment.	Parts per million of soluble organic matter.
1	Acetic-acid-treated soil+10 per cent of sodium sulphate.....	120
2	Acetic-acid-treated soil+10 per cent of sodium sulphate+0.4 per cent of calcium carbonate.....	200
3	Acetic-acid-treated soil+10 per cent of sodium sulphate+0.4 per cent of calcium carbonate saturated with carbon-dioxid gas at atmospheric pressure.....	60

The fact that the presence of calcium carbonate increases the solubility of the organic matter indicates that the sodium sulphate is acting upon calcium carbonate with the formation of the normal sodium carbonate, and this is acting upon the organic matter of the soil. When carbon dioxid is present in excess, the reaction forms sodium bicarbonate, which shows little action upon organic matter. This experiment was repeated with sodium chlorid, with practically the same results.

ACTION OF SODIUM CARBONATE AND SODIUM BICARBONATE UPON ORGANIC MATTER

Having demonstrated the fact that in the soil sodium salts react with lime to form sodium carbonate and this attacks the organic matter of the soil, the pure salts sodium carbonate and sodium bicarbonate were added in varying concentrations to the station soil and brought to equilibrium. Portions of the solutions were withdrawn and titrated for carbonates and bicarbonates, and determinations were made of the

soluble organic matter. These are shown in Tables XXXIX and XL, and in figure 22.

The difference between the amount of sodium carbonate added to the solution and that shown by the titration after equilibrium has been established is indicated in the column "Lost" in Table XXXIX. By subtracting the control, No. 1, fron the others and dividing the sodium carbonate "lost" into the parts per million of organic matter brought into solution, the parts per million of organic matter brought into solution for every 100 parts per million of sodium carbonate lost are obtained. This shows the relative solvent action of sodium carbonate when acting in weak and in fairly strong solutions. Contrary to what one might expect, this experiment seems to show that a unit of sodium carbonate is nearly 10 times more effective in a strong concentration than in a weak one. It is well known, however, that, when sodium carbonate is added to the soil, a part of it becomes fixed—that is, it is absorbed by the soil grains or is combined with the silicates or other like bodies of the soil. This fixation would remove in absolute amounts almost as much from a weak solution as from a moderately strong one, and would, of course, leave relatively less free sodium carbonate in the weak solution than in the strong one to act upon the organic matter. The carbon dioxid existing in the soil would also convert a small amount of sodium carbonate into sodium bicarbonate. This action would be almost equal in the weak and the strong solutions. The sodium bicarbonate thus formed would be almost negligible, so far as its action upon the organic matter is concerned.

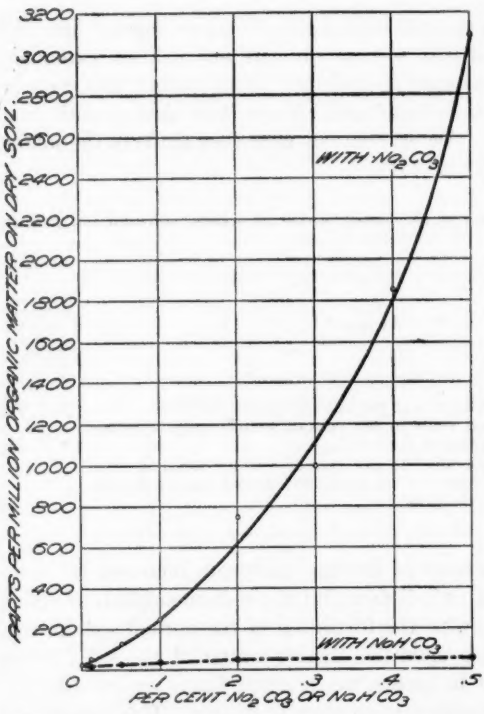

FIG. 22.—Graphs showing the solubility of organic matter in a soil in sodium-carbonate and sodium-bicarbonate solutions.

TABLE XXXIX.—*Solubility of organic matter in sodium-carbonate solutions*

Solution No.	Percentage of sodium carbonate.			Parts per million of organic matter on soil.	Parts per million after subtracting No. 1 (control) from others.	Parts per million of organic matter brought into solution for every 100 parts per million of sodium carbonate lost.
	Added.	Recovered.	Lost.			
1	0.0	0.0	0.0	30	0	0
2	.01	Trace.	.01	60	30	30
3	.05	.019	.031	130	100	32
4	.10	.051	.049	250	220	45
5	.20	.117	.083	750	720	87
6	.30	.212	.088	1,000	970	110
7	.40	.297	.103	1,875	1,854	179
8	.50	.390	.110	3,100	3,070	279

TABLE XL.—*Solubility of organic matter in sodium bicarbonate*

Solution No.	Percentage of sodium bicarbonate.		Parts per million of organic matter on soil.	Parts per million after subtracting No. 1 (control) from others.
	Added.	Recovered.		
1	0.00	0.005	24	0
2	.01	.015	24	0
3	.05	.059	30	6
4	.10	.105	44	20
5	.20	.193	60	36
6	.50	.445	70	46

As the soils contain some bicarbonates, more was recovered in some cases than was added. Sodium bicarbonate seemed to exert little effect upon the organic matter of the soil.

EFFECT OF SODIUM SALTS UPON THE SOLUBILITY OF CALCIUM CARBONATE IN SOILS

In treating a soil with a sodium-chlorid solution, with and without calcium carbonate, and analyzing it for lime in the usual way, a striking phenomenon is to be noticed. In Table XLI is shown the total amount of water-soluble lime calculated to calcium carbonate obtained by two different methods of analysis. In the first method the total lime was precipitated as calcium oxalate and weighed as calcium oxid. In the second method the bicarbonates in the solution were titrated with standard acid and the titrations calculated to calcium carbonate.

TABLE XLI.—*Solubility of calcium carbonate in soils*

Solution No.	Percentage of sodium chlorid.	Total water-soluble calcium oxid.			HCO_3 titrations.		
		Soil control.	Soil+2 per cent calcium carbonate.	Difference.	Soil control.	Soil+2 per cent calcium carbonate.	Difference.
1	0	105	273	168	150	450	300
2	1	714	942	228	75	525	450
3	5	1,113	1,470	357	50	525	475
4	10	1,239	1,638	399	0	425	425
5	20	1,258	1,783	525	0	250	250
6	30	1,239	1,764	525	0	75	75

By subtracting the water-soluble lime extracted from the controls from the lime recovered from soil to which calcium carbonate had been added, a difference is obtained, representing the effect of the application of calcium carbonate. In the same way are subtracted the bicarbonate determinations and a difference secured, also representing the effect of the calcium carbonate. It will be seen that there is a regular increase in the case of the total water-soluble lime, and, first a rise, then a drop, in the case of the bicarbonates. The calcium carbonate has gone into solution but is not present as a carbonate or bicarbonate. The presence of sodium chlorid in the higher concentrations seems to be forcing back the solubility of calcium as a bicarbonate. This is also true with sodium nitrate and sodium sulphate.

ALKALI CRUSTS IN IRRIGATED REGIONS

In many of the irrigated districts in southern California, especially around Riverside and Corona, the so-called crusts or efflorescence of alkali salts is frequently noticed on the surface of the soil. These crusts appear after each irrigation as a light, fluffy, brown efflorescence, particularly along the edge of the irrigation furrow. They are not crusts, except in the popular conception of the term, in that they do not harden the surface of the soil; they are also to be distinguished from the black, gummy crust formed by black alkali, and from the crystalline crust of the other sodium salts constituting white alkali.

They are usually dissolved by each irrigation and carried down into the soil only to be returned to the surface in a few days by the upward movement and evaporation of the water. This upward and downward movement is continued throughout the season until the crusts are finally dissolved by the winter rains and carried down to some depth into the soil or off by drainage. Unless the winter rains are unusually heavy, the crusts usually appear again in the spring after the first irrigation. Both the crusts themselves and their water extracts are extremely toxic to Citrus seedlings, the toxicity being entirely out of proportion to the known toxicity of the inorganic salts that make up the solution.

Four samples of these crusts were collected by scraping the surface soil, and extracts were made by shaking them with distilled water and filtering off the soil through Pasteur filters. These solutions were then evaporated to dryness, the residue was dried at 100° F., and portions were taken for analysis. These analyses are given in Table XLII expressed as ions, and also empirically combined as salts, on the basis of the dry water-soluble material.

TABLE XLII.—*Percentage composition of water-soluble material*

GROVE A, RIVERSIDE.				HIGHGROVE GROVE.			
Ions.		Combined as salts.		Ions.		Combined as salts.	
Constituent.	Per cent.	Constituent.	Percent.	Constituent.	Per cent.	Constituent.	Per cent.
Ca	9.36	$CaSO_4$	17.80	Ca	11.82	$CaSO_4$	18.38
Mg	1.52	$Ca(NO_3)_2$	16.95	Mg	2.47	$Ca(NO_3)_2$	26.05
Na	5.01	$MgCl_2$	1.55	K	1.70	$Mg(NO_3)_2$	15.01
K	7.09	$Mg(NO_3)_2$	7.35	Na	7.98	KCl	3.16
SO_4	12.58	KCl	8.00	SO_4	13.03	$NaNO_3$	9.34
NO_3	19.02	$KHCO_3$	3.40	Cl	5.98	NaCl	7.45
Cl	4.99	K_2CO_3	2.42	NO_3	39.30	$NaHCO_3$	3.66
CO_3	1.79	Na_2CO_3	1.33	HCO_3	2.66	Na	1.50
HCO_3	2.04	Na	4.58			Organic matter.	15.06
		Organic matter.	36.70				
CORONA GROVE.				GROVE B, RIVERSIDE.			
Ca	13.11	$CaSO_4$	13.13	Ca	14.72	$CaSO_4$	5.72
Mg	1.70	$Ca(NO_3)_2$	37.88	Mg	2.14	$Ca(NO_3)_2$	53.51
K	2.32	$Mg(NO_3)_2$	5.75	K	1.41	$Mg(NO_3)_2$	13.02
Na	6.22	$MgCl_2$	3.01	Na	3.76	KCl	2.70
SO_4	9.30	KCl	4.43	SO_4	4.04	$NaNO_3$	.04
Cl	9.15	NaCl	7.93	NO_3	51.45	NaCl	2.83
NO_3	33.38	Na_2CO_3	1.46	Cl	3.00	Na_2CO_3	.43
CO_3	.83	$NaHCO_3$	1.54	CO_3	.17	$NaHCO_3$	1.06
HCO_3	1.12	Na	2.04	HCO_3	.77	Na	2.21
		Organic matter.	22.93			Organic matter.	18.50

When the bases are combined with the acids, beginning with calcium, and following with magnesium, potassium, and sodium in order, it will be noticed that there is some sodium left over uncombined. This probably existed in part in combination with the organic acids, which were not determined. The sodium no doubt at one time existed as sodium carbonate and had attacked the organic matter of the soil; therefore, at the time of the analysis, it was partly locked up in organic combination. A high percentage of soluble organic matter was to be expected. A high percentage of calcium nitrate is also noticeable. This is due to the fact that active nitrification had been going on in the soil with the formation of nitric acid, which had combined with the calcium carbonate of the soil, with the formation of calcium nitrate. Theoretically these crusts could not form in a soil containing no carbonates.

Several samples of soil were taken from lemon groves, good and poor, without and with the alkali crust. These soils were placed in 6-inch pots and planted with very young lemon seedlings. In every case the soils from the good groves gave good plants, while the soils from the poor groves, the groves which had the alkali crust, gave poor plants. Two representative plants are shown in Plate 62, B. Both of these soils were taken from the feeding zone (second foot); the poor one, therefore contained little of the alkali crust which was, at the time of sampling, principally on the surface, but certainly enough to affect the lemon seedlings. The analysis of the crust appearing on the surface of this soil is given in Table XLII, Corona grove.

The high percentage of soluble organic matter was the most striking feature of the analysis of the water-soluble salts, constituting the crusts. This amounted to as high as 36 per cent of the dry material and was sufficient to give color to all the solutions, ranging from brown to nearly black. It will be shown later that, with the exception of sodium carbonate, none of the salts likely to occur has an appreciable effect in bringing the organic matter of the soil into solution. In fact, most of the lime salts seem either to be inert in this respect or else to exert a protective action upon the organic matter. The action of sodium carbonate upon organic matter is pronounced.

None of the crusts would react with phenolphthalein; neither did their solutions give any reaction for sodium carbonate, until they had been boiled for some time. This showed that no sodium carbonate was present at the time of sampling, but the color of the solution indicated, if it did not prove, that sodium carbonate had at one time been present.

ORIGIN OF BARREN, OR "SLICK," SPOTS

The fact that a very toxic compound is formed by the union of sodium carbonate and organic matter goes far to explain many of the phenomena noticed in the field. At North Platte, Nebr., in the river valley, there are many barren spots in the grain and alfalfa fields that are probably due to this cause. These spots are usually absolutely barren, and are surrounded by luxuriant growths of grain or alfalfa. By the casual observer these are attributed to excessive amounts of sodium sulphate or sodium chlorid, but a chemical examination of the soils showed little difference in the inorganic salt content of the good and poor spots. These spots are typical of a thousand that are scattered over the arid and semi-arid regions of the West. The predominating alkali at North Platte is sodium sulphate. The soil is rich in calcium carbonate and humus, and the conditions are ideal for the reaction before described. When extracts from the good and poor spots from this vicinity are made, the poor spots can be readily detected by the deep color of the solutions, owing to the organic matter, and by a characteristic "soapy," or alkali, odor.

In a recent bulletin of the Utah Experiment Station (4) an attempt was made to determine the amount of alkali necessary to prohibit the growth of certain field crops. Some barren spots, like those described at North Platte, were selected and comparisons made between these spots and good places in the same or adjoining fields, and the assumption was made that the barrenness of the poor spots was due to the common "alkali" salts. In the light of the results here presented, the present writer seems justified in suggesting the possibility that conditions other than alkali might enter into the barrenness of these spots.

The difference in the solubility of the salts formed in the reactions between the sodium salts and calcium carbonate, and the difference in their rate of movement through the soil is responsible in a large measure for the accumulation of the different salts on the surface in different places. We may have "black alkali" spots, in which sodium carbonate predominates, or the so-called "slick spots," in which calcium carbonate predominates, or the so-called "niter spots," in which calcium nitrate predominates.

The presence of black alkali, or sodium carbonate, in such small amounts as 0.1 to 0.05 per cent renders some soils unfit for cultivation. The injurious effects on field crops, generally attributed to sodium carbonate, is, as has been shown, often out of proportion to what might be expected from results obtained from studies in pure solutions. In the presence of the organic matter and silica of the soil the sodium carbonate is likely to enter into combination not only with the organic matter but with the silica of the soil, as fast as it is formed. In such cases its very presence is often overlooked, existing, as it does, in such small amounts. Enough carbon dioxid is usually added with the distilled water used in making the soil extract for analysis to convert the sodium carbonate to bicarbonate. It thus fails to show color with phenolphthalein, and the soil is said to contain no sodium carbonate. It does exist, however, in what might be termed a transition state between its formation and its combination with the silica or organic matter.

In its action upon the finely divided material of the soil the characteristic puddling or cementing is likely to take place. This action usually occurs in spots and is not often extended over wide continuous areas. Many of the barren spots in the semiarid areas are probably due not to the accumulation of alkali, but to the cementing action of sodium carbonate. The soil puddles, will not take water, and thereby soon becomes barren, the barrenness being due primarily to lack of water. Some excellent work has been done by Headley, Curtis, and Scofield (5) at Fallon, Nev., along this line.

In the humid regions the accumulation of injurious compounds in the soil is not a question of much importance. This is being taken care of by the rains, which make the movement of the soil water downward through the subsoil. The injurious bodies are then leached out. In the

arid and semiarid regions, however, with slight rainfall, under conditions of irrigation, little or no drainage can take place. The injurious compounds are then likely to accumulate in the soil. It seems to the writer that the accumulation of such combination of salts and organic matter as are here described should be dreaded. Such formations as these might well be considered the secondary stage of alkali accumulation, described in the first part of this paper.

It is an old adage in greenhouse work, "Water the pots until the water runs out of the bottom." In other words, to get the best results a little drainage is always necessary. In irrigation agriculture, however, when there is a scarcity of water, enough is not usually applied to cause any drainage, even when there is a porous soil with sandy or open subsoil. Under these conditions, if the winter rains are not heavy enough to produce the desired effect, the injurious products of decomposition are likely to accumulate year after year until they reach an amount that will seriously interfere with agriculture.

It seems to be a fact that good Citrus crops usually follow heavy winter rains. The rejuvenation, or "coming back," of many orchards may well be attributed to this. This was particularly noticeable in the Riverside area in the season of 1916 after the unusually heavy rains of the preceding winter. The groves probably did not "come back" on account of any change in the cultural treatment, as was thought by many, but on account of the removal of injurious compounds from the soil.

PROTECTIVE ACTION OF SODIUM CHLORID AND SODIUM SULPHATE UPON THE ORGANIC MATTER OF THE SOIL IN PRESENCE OF SODIUM CARBONATE

It has already been shown that sodium chlorid and sodium sulphate both have a slight solvent action upon the organic matter of the soil. This is especially true of sodium sulphate. In the presence of sodium carbonate, however, a remarkable phenomenon is to be observed. Both salts tend to reduce the solvent action of sodium carbonate.

The solvent action of sodium carbonate, which is far greater than that of the other sodium salts, is due in all probability to the ionized OH radical. Sodium carbonate being a strong base combined with a weak acid has a decided tendency to hydrolyze—that is, to combine with water in the following manner: $Na_2CO_3 + H_2O \rightleftarrows 2NaOH + H_2CO_3$. The sodium hydrate formed in this reaction will in turn ionize into Na and OH. The sodium hydrate formed by the hydrolysis, then, is directly responsible for its caustic action upon the organic matter of the soil, and its degree of ionization is a measure of it.

By introducing a salt with a common ion into a weak solution of sodium carbonate the ionization may be so forced back as no longer to show color with phenolphthalein. The sodium carbonate as such will still remain in solution, but will not be hydrolyzed. In this way sodium

chlorid, sodium sulphate, and sodium nitrate may under field conditions exert a protective action upon the organic matter of the soil from the solvent action of "black alkali."

A 0.5 per cent solution of sodium carbonate was prepared and used to make up soil extracts in the regular proportion of 1 of soil to 5 of solution. Graduated amounts of sodium chlorid and sodium sulphate were added to the solutions, which were brought to equilibrium. The amount of organic matter which went into solution in each instance is indicated in Tables XLIII and XLIV, and in figure 23.

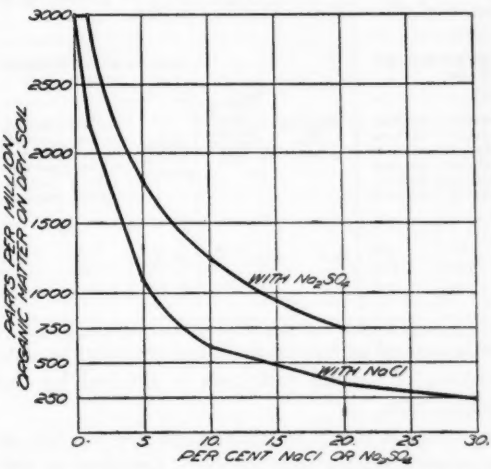

FIG. 23.—Graphs showing the protective action of sodium chlorid and sodium sulphate upon organic matter of the soil in the presence of sodium carbonate.

A rapid decrease is noticed in the amount of organic matter dissolved by 0.5 per cent of sodium carbonate when either of the other sodium salts are introduced into the solution. This action is more marked with sodium chlorid than with sodium sulphate. The neutral salts seem to be acting in a protective rôle upon the organic matter of the soil.

TABLE XLIII.—*Solubility of organic matter in sodium carbonate in the presence of sodium chlorid*

Solution No.	Percentage of sodium carbonate.	Percentage of sodium chlorid.	Parts per million of organic matter on dry soil.	Solution No.	Percentage of sodium carbonate.	Percentage of sodium chlorid.	Parts per million of organic matter on dry soil.
1.....	0.5	0	3,000	4.....	0.5	10	625
2.....	.5	1	2,200	5.....	.5	20	350
3.....	.5	5	1,100	6.....	.5	30	250

TABLE XLIV.—*Solubility of organic matter in sodium carbonate in the presence of sodium sulphate*

Solution No.	Percentage of sodium carbonate.	Percentage of sodium sulphate.	Parts per million of organic matter on dry soil.	Solution No.	Percentage of sodium carbonate.	Percentage of sodium sulphate.	Parts per million of organic matter on dry soil.
1.....	0.5	0	3,000	4.....	0.5	10	1,250
2.....	.5	1	3,000	5.....	.5	20	750
3.....	.5	5	1,800				

In Table XLV is shown the effect of sodium carbonate upon the organic matter of the soil, acting, first alone in amounts from 0 to 1 per cent, second in a 10 per cent solution of sodium chlorid, and third in a 10 per cent solution of sodium sulphate.

TABLE XLV.—*Solubility of organic matter in sodium carbonate in the presence of 10 per cent solutions of sodium chlorid and sodium sulphate*

Solution No.	Percentage of sodium carbonate.	Parts per million of organic matter.			Solution No.	Percentage of sodium carbonate.	Parts per million of organic matter.		
		Sodium carbonate alone.	Sodium carbonate + 10 per cent sodium chlorid.	Sodium carbonate + 10 per cent sodium sulphate.			Sodium carbonate alone.	Sodium carbonate + 10 per cent sodium chlorid.	Sodium carbonate + 10 per cent sodium sulphate.
1.....	0.0	30	60	420	4.....	0.50	3,000	650	1,500
2.....	.1	400	240	800	5.....	.75	3,700	800	1,800
3.....	.25	800	500	1,000	6.....	1.00	5,250	1,000	2,500

The same phenomenon is noticed as was shown in the preceding experiment; the destructive action of sodium carbonate is checked by the presence of the other sodium salts.

In Table XLVI and figure 24 is shown to what extent the reaction of sodium carbonate upon organic matter is reversible. Solutions of soil

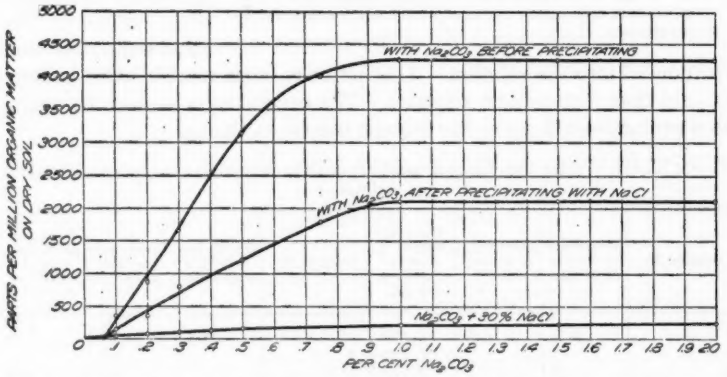

FIG. 24.—Graphs showing the organic matter dissolved from soil by sodium carbonate and afterwards precipitated by sodium chlorid.

were made with varying concentrations of sodium carbonate and the soil filtered off. Determinations of the organic matter were then made upon the solutions. An excess of sodium chlorid was then added to each of the solutions, the solution boiled, and the resulting precipitate filtered off. Determinations of the organic matter were again made on the filtrates. These final readings represented the amount of organic matter that went into solution with sodium carbonate, but which could not be precipitated out with sodium chlorid.

The solubility of organic matter in varying amounts of sodium carbonate when sodium chlorid was in the solution is also given.

TABLE XLVI.—*Solubility of organic matter in sodium-carbonate solutions*

Solution No.	Percentage of sodium carbonate added.	Parts per million organic matter on dry soil.			Solution No.	Percentage of sodium carbonate added.	Parts per million organic matter on dry soil.		
		Before precipitating with sodium chlorid.	After precipitating with sodium chlorid.	Solubility in sodium carbonate in presence of 30 per cent of sodium chlorid.			Before precipitating with sodium chlorid.	After precipitating with sodium chlorid.	Solubility in sodium carbonate in presence of 30 per cent of sodium chlorid.
1.....	0.1	360	140	40	5.....	.75	4,000	1,800	.....
2.....	.2	875	350	80	6.....	1.00	4,250	2,100	200
3.....	.3	1,650	800	100	7.....	1.50	4,250	2,100	220
4.....	.5	3,125	1,200	160	8.....	2.00	4,250	2,100	240

From the above table it will be noted that after the organic matter of the soil has once been brought into solution by the sodium carbonate, approximately one-half can be reprecipitated with sodium chlorid.

From all the results so far obtained it would seem that the injurious effect of sodium carbonate in its action upon the organic matter of the soil rests in that portion of the salt which is hydrolyzed into sodium hydrate. The rate of hydrolysis of sodium carbonate in pure solution and in the presence of sodium salts may be measured by means of the saponification of ethyl acetate. Ten c. c. of ethyl acetate were therefore put into 150 c. c. of 0.4 per cent of sodium carbonate, using pure water and increasing amounts of sodium chlorid. After standing with frequent shaking, for 20 minutes, a portion of the solution was withdrawn and titrated against standard acid, using phenolphthalein as an indicator. This titration was repeated after 40, 60, and 100 minutes, respectively. The amount of unsaponified sodium carbonate was thus determined, and by subtracting this from the total amount in the original solution, the quantity of saponified sodium carbonate was determined. This experiment was repeated with sodium sulphate, using a 0.49 per cent sodium carbonate. The results are shown in Tables XLVII and XLVIII and in figures 25 and 26.

TABLE XLVII.—*Saponification of ethyl acetate by sodium carbonate in the presence of sodium chlorid*

Solution No.	Per centage of sodium chlorid.	Percentage of sodium carbonate saponified in—				Solution No.	Per centage of sodium chlorid.	Percentage of sodium carbonate saponified in—			
		20 minutes.	40 minutes.	60 minutes.	100 minutes.			20 minutes.	40 minutes.	60 minutes.	100 minutes.
1.....	0	0.220	0.294	0.315	0.347	4.....	20	0.093	0.114	0.125	0.163
2.....	5	.190	.209	.230	.269	5.....	30	.061	.071	.082	.125
3.....	10	.135	.167	.188	.230						

TABLE XLVIII.—*Saponification of ethyl acetate by sodium carbonate in the presence of sodium sulphate*

Solution No.	Percentage of sodium sulphate.	Percentage of sodium carbonate saponified in—			
		20 minutes.	40 minutes.	60 minutes.	100 minutes.
1	0	0.318	0.392	0.428	0.445
2	10	.212	.275	.297	.318
3	20	.159	.212	.233	.254

These two tables clearly show to what degree the presence of sodium chlorid and sodium sulphate holds back the hydrolysis of sodium carbonate. Under field conditions we might expect black alkali to be more

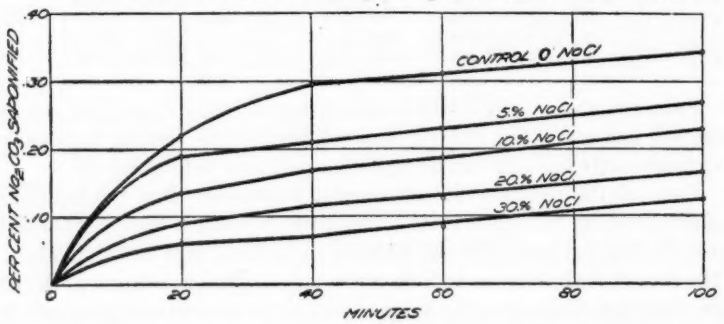

FIG. 25.—Graphs showing the saponification of ethyl acetate by sodium carbonate in the presence of sodium chlorid.

caustic when acting alone than when in the presence of either sodium chlorid or sodium sulphate.

In judging the amount of organic matter by the color of the solution in this and in preceding experiments the writer realizes that the method is far from satisfactory and that the data obtained do not represent the absolute amount of organic matter in solution. But the error in the determination would quite likely remain fairly constant in the different experiments, and, therefore, comparable results could be reasonably expected. This was all that was hoped for.

EFFECT OF LIME HARDPAN UPON FORMATION OF BLACK ALKALI

It is a well-known fact that a hardpan frequently accompanies black alkali. It has been commonly supposed that the black alkali is responsible for the hardpan, whereas in many cases the opposite may be true. If the hardpan is simply a puddled condition of the soil, the puddling might readily be brought about by the black alkali. In the case of the calcareous hardpan, with a sodium salt present, even if the top soil is not calcareous, black alkali might readily be produced in the following

manner. Suppose sodium chlorid is deposited on the surface in a crystalline form, and rain or irrigation water dissolves this and carries it down in a fairly concentrated form until the hardpan is reached. Here the evaporation of the water may further increase the concentration of the salt and the action upon the lime carbonate may take place in a rather concentrated solution. The black alkali, together with the soluble lime salt formed and the excess of the sodium chlorid is then, or thereafter, brought to the surface by the capillary action of the water. Here the sodium chlorid may again crystallize out upon the surface and be ready for the next rain or irrigation to carry it down through the soil for a further action upon the calcareous hardpan. This phenomenon was strikingly brought out in the experiment, illustrated in Plate 62, C. Two lantern chimneys were filled with pure quartz sand, and during the

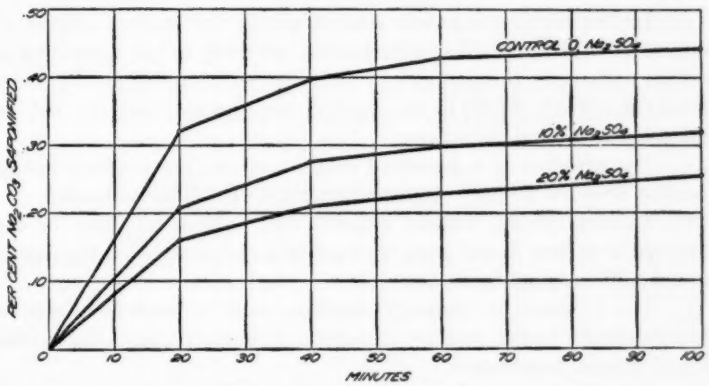

FIG. 26.—Graphs showing the saponification of ethyl acetate by sodium carbonate in the presence of sodium sulphate.

filling a thin layer of calcium carbonate was introduced into each. In No. 1 the bottom was stopped up and the layer of calcium carbonate placed at the lower end of the column; in No. 2 the calcium carbonate was placed about midway, and the bottom of the chimney closed with a strip of linen. No. 1 was then kept watered from the top with a 10 per cent solution of sodium sulphate, while No. 2 was placed in a large evaporating dish, containing some of the same sodium-sulphate solution. These chimneys illustrated two field conditions: One in which the calcareous hardpan is at the lower edge of the moisture plane, where under field conditions it would exist, the water having to penetrate the full depth of the soil to reach it; the other where the hardpan lies near the surface, the water, entering below, has to pass through the layer in order to reach the surface.

After several days sodium carbonate appeared on the surface of both chimneys of sand. In the case of No. 1, the sodium sulphate penetrated the sand until the calcium carbonate was reached, the reaction between

the two salts then took place ($Na_2SO_4 + CaCO_3 \leftrightarrows Na_2CO_3 + CaSO_4$), and the products of the reaction were brought to the surface by capillarity. In the case of No. 2, the sodium sulphate, coming up through the sand by capillarity, had to pass through the thin layer of calcium carbonate. At this point the same reaction took place, and the sodium carbonate was brought to the surface.

This experiment illustrates what often takes place in the field and is a possible explanation of why a lime hardpan almost invariably accompanies black alkali. The reverse of this, however, is not true. Black alkali does not always accompany hardpan, for the obvious reason that sodium chlorid or sodium sulphate are not always present in sufficient amounts in the soil or in the irrigation water to bring about the reaction.

CONCLUSIONS

(1) In the reaction between sodium nitrate (or sodium chlorid or sodium sulphate) and calcium carbonate, resulting in the formation of sodium carbonate, the presence of relatively small amounts of calcium nitrate or calcium chlorid in the reaction impedes and may prevent the formation of sodium carbonate.

(2) The presence of a saturated solution of calcium sulphate in this reaction does not entirely stop the formation of sodium carbonate.

(3) Sodium nitrate, sodium chlorid, and sodium sulphate in the presence of carbon dioxid react with calcium carbonate with the formation of sodium bicarbonate.

(4) The presence of relatively small amounts of calcium nitrate or calcium chlorid in this reaction impedes and finally prevents the formation of sodium bicarbonate.

(5) The presence of calcium sulphate has no effect in preventing the formation of sodium bicarbonate when sodium sulphate or a mixture containing sodium sulphate reacts with calcium carbonate.

(6) A field application of gypsum will probably have no effect in overcoming black alkali if the soil already contains soluble sulphates in appreciable amounts, or the irrigation water contains these salts.

(7) Sodium nitrate, sodium chlorid, and sodium sulphate increase the solubility of calcium carbonate in the soil.

(8) Sodium nitrate, sodium chlorid, and sodium sulphate react with calcium carbonate in the soil with the formation of sodium carbonate ("black alkali").

(9) Sodium carbonate, formed by the above reaction, decomposes the organic matter of the soil.

(10) Calcium carbonate has a slightly destructive action upon the organic matter of the soil.

(11) Sodium carbonate is much more destructive upon organic matter than sodium bicarbonate.

(12) The alkali crusts that accumulate upon the soil in some irrigated regions are due in part to the action of sodium salts upon calcium carbonate with the formation of sodium carbonate.

(13) Barren, or "slick," spots are often due to the action of sodium nitrate, sodium chlorid, or sodium sulphate upon calcium carbonate with the formation of sodium carbonate.

(14) Sodium chlorid and sodium sulphate have a protective action upon organic matter in the presence of sodium carbonate.

(15) A calcareous hardpan often produces black alkali.

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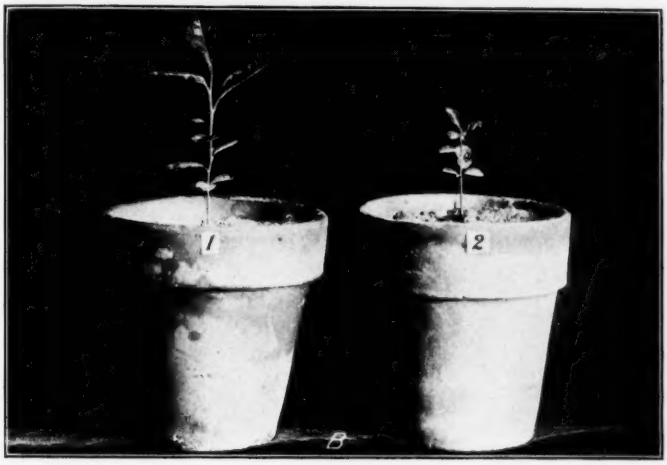
PLATE 62

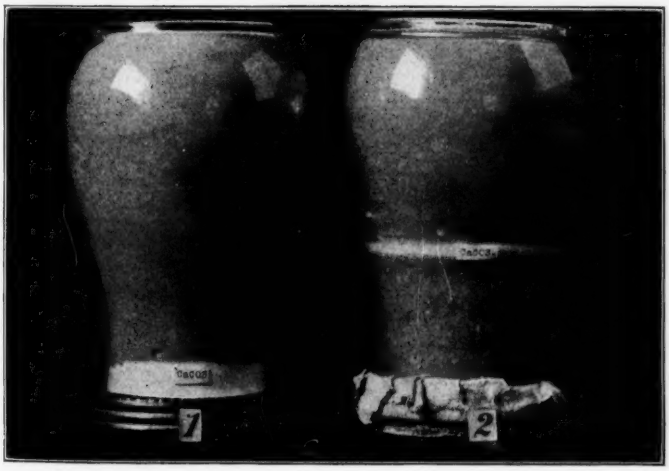
A.—One-year-old lemon seedlings, showing the effect of additions of lime and manure to the soil: Pot 1, soil untreated; pot 2, 2 per cent of calcium carbonate added; pot 3, 1 per cent or manure added; pot 4, 1 per cent of manure and 2 per cent of calcium carbonate.

B.—Two-and-one-half-month-old lemon seedlings, showing the effect of alkali crust on ground: Pot 1, good grove, no crust; pot 2, poor grove, crust on surface.

C.—Reservoirs, showing the effect of a lime hardpan upon the formation of black alkali: 1, Hardpan ($CaCO_3$) at the lower edge of the moisture plane; 2, hardpan midway soil column.

1
2
3
4
A


1
2
B


1
2